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**THE ROLE OF NITROGEN ON THE
FLOTATION PERFORMANCE OF A
COMPLEX SULPHIDE ORE**

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A dissertation submitted to the Faculty of Engineering and the Built Environment,
University of Cape Town, in fulfilment of the requirements for the degree of
Master of Science in Engineering.

Cape Town, August 2000

DECLARATION

I declare that this dissertation is my own work. It is being submitted for the degree of Master of Science in Engineering at the University of Cape Town, and has not been submitted before for any degree or examination at this or any other university.

Signed by candidate

Imraan Bacus

This thesis is dedicated to the memory of my father, Yusuf Bacus, and to my loving mother, brothers and sisters who have stood by me for the past 26 years.

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SYNOPSIS

This thesis focuses on the role of nitrogen on flotation performance of a sulphide PGM ore.

Merensky ore obtained from Impala Platinum mine, Rustenburg, was used in laboratory batch flotation tests. Nitrogen addition was implemented during the conditioning and / or flotation stages of the test. In order to further evaluate the consistency of the role of nitrogen, tests were conducted using both stainless steel and mild steel as the milling media during the milling step prior to batch flotation.

Specifically, the objectives of this thesis were as follows:

To investigate the effect of nitrogen on the metallurgical flotation performance of the complex sulphide ore, as measured by mineral recoveries and grades of the major sulphide elements, copper, nickel and iron. These represent the major sulphides present in the ore; chalcopyrite (Cu), pentlandite (Ni) and pyrrhotite (Fe, as an approximate representative since Fe occurs in pyrrhotite, chalcopyrite, pentlandite as well as non-sulphide gangue).

Secondly, to develop an understanding of the mechanisms of nitrogen addition on the relevant sub processes and interactions in froth flotation. The elucidation of these mechanisms was carried out with aid of complementary investigative studies which focused on the issues relating to the mechanistic role of nitrogen in flotation, as identified by the literature review.

The first of these involved the evaluation of the role of nitrogen on the pulp chemical environment. The pulp chemical environment is defined here as the water - ore - reagent medium in which the valuable particle resides during the froth flotation process. Profiles of pH, temperature, dissolved oxygen (DO) and oxidation reduction potential (ORP, measured with a Pt - Ag/AgCl electrode) were recorded for each flotation test so as to monitor the changes in the pulp chemical environment, as a response to changes in milling media, reagent addition and gas addition.

The second complimentary investigation involved the evaluation of the role of nitrogen on mineral surface oxidation. This involved the measurement of the level of metal hydroxide on the minerals' surface with a technique employing EDTA (ethylene diamine tetra acetic acid) for the purposes of extraction. This was to ascertain whether the addition of nitrogen during flotation tests resulted in reduced mineral surface oxidation either as a result of the direct effect of nitrogen or an indirect effect via galvanic

interaction protection mechanisms.

The final complimentary investigation involved an evaluation of the role of nitrogen on the collector-mineral and collector-mineral-activator interactions. This entailed the measurement of residual xanthate by UV spectroscopy. This was to ascertain whether any change in flotation response with nitrogen addition was attributable to a shift in the collector-activator-mineral interaction scheme.

During batch flotation, it was found that nitrogen gas added during the conditioning stage lead to a 16% recovery benefit for the nickel minerals (pentlandite), with no benefit to copper (chalcopyrite) and iron (pyrrhotite), when stainless steel media was used in the preparation of pulp during the milling stage. Previous studies suggested that the improvement in nickel recovery could be due to reduction of hydrophilic species on the mineral surface, as a consequence of the low ORP and DO levels associated with nitrogen addition. Tests (ex-situ) measuring the level of surface hydroxides under simulated test conditions found that a lower level of surface hydroxides were removed from the nickel minerals' surface when the pulp was conditioned with nitrogen. At the same time, however, the magnitude of the change in the level of surface hydroxides was not deemed sufficient to be solely responsible for the observed recovery increase. The results of further investigations on the role of nitrogen on collector – activator – mineral relationships indicated that the presence of nitrogen in conditioning significantly decreased the stoichiometric ratio of the xanthate to copper reaction. This is an important observation, and implies a fundamental change in the reaction mechanism between the mineral and collector in the presence of copper sulphate activator during nitrogen conditioning.

Additionally, nitrogen used in BOTH the conditioning and flotation stages reduced the recoveries of copper (chalcopyrite) by 10% and iron (pyrrhotite) by 5%, but NOT nickel (pentlandite). This indicates that dithiolate formation, (or equivalent DO and ORP levels), is required for iron (pyrrhotite) and copper (chalcopyrite) recovery, but not necessarily for nickel (pentlandite) recovery. This is supported by Kelebek (1993) who showed similar trends for flotation results. In this instance, pentlandite's ability to develop hydrophobicity under oxygen free conditions is sited as the reason for the observed behaviour of nickel recoveries being unaffected by the addition of nitrogen during both conditioning and flotation. Furthermore, the literature suggests that dixanthogen is the active collector for chalcopyrite and pyrrhotite minerals, which confers with the hypothesis that nitrogen blanketing of the flotation system results in hindered dithiolate formation, and thus reduced performance of minerals dependant on it.

Nitrogen conditioning did not benefit flotation performance when used in conjunction with mild steel milling media. Tests measuring the level of ferrous ions indicate that there is tenfold more Fe present as hydroxides after mild steel milling compared to after stainless steel milling, indicating that the pulp chemistry is significantly different when mild steel media is employed. The subsequent froth stabilisation that occurs as a direct result of these hydroxy species may lead to other effects that swamp out any subtle changes and benefits in the pulp zone with regard to surface chemistry during nitrogen conditioning.

Finally, the complimentary investigations on the mineral-activator-collector interaction and on the levels of mineral surface oxidation show interesting phenomena that justify further investigation via more direct approaches. FTIR (Fourier Transform Infrared Spectroscopy) or TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy) techniques are recommended for further investigation of the role of nitrogen in flotation.

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GLOSSARY

PGM	- Platinum group metal
ΔG	- Change in Gibbs free energy
γ_{LV}	- Tension of the liquid-vapour interface
θ	- Contact angle between the liquid - vapour and liquid solid interface
SIBX	- Sodium Iso-Butyl Xanthate (collector)
nC4-DTP	- normal Butane Di-thio Phosphate (collector)
SF7000	- Proprietary frother (manufactured by Senmin)
IMP4	- Guar type depressant
DO	- Dissolved oxygen
ORP	- Oxidation reduction potential
E_h	- Potential relative to standard hydrogen electrode
$E_{Ag/AgCl}$	- Measured potential with reference to a standard Ag/AgCl electrode
N_2	- Nitrogen
X_2	- Di-xanthogen (also referred to as di-thiolate)
EDTA	- Ethylene Diamine Tetra Acetic Acid
Cu	- Copper
Ni	- Nickel
Fe	- Iron
SS	- Stainless steel
MS	- Mild steel
NA	- Denotes a flotation test where nitrogen gas was added to the cell during the conditioning stage (after reagents were added)
NF	- Denotes a flotation test where nitrogen was used as the flotation gas instead of air

1. INTRODUCTION

Froth flotation is widely used as a means of mineral beneficiation in South Africa's platinum industry. Essentially, crushed ore is processed to concentrate the valuables before further processing and smelting. This processing, employing chemicals that alter the minerals' hydrophobicity and thus providing the mechanism for concentration, is known as froth flotation.

The process consists of three main steps; crushing and grinding of the ore to a suitable size to ensure liberation of valuable minerals, conditioning the crushed ore slurry with reagents, and finally, removal of the valuables by flotation with a gas, usually air.

The crushed ore, distributed between small stone sized particles and small rocks measuring 15-20 cm in diameter, is fed to mills where the particles are reduced to a specified size, typically < 200 mm. The milling process is intended to physically liberate the valuable minerals present in the ore, as well as render them small enough for subsequent flotation by a gas bubble. Milling and grinding is generally carried out using either balls or rods, and the grinding media is made from various qualities of steel ranging from stainless steel to mild steel material. For sulphide flotation, as is the case in this study, the type of grinding media plays an important role in the subsequent flotation process, since it influences the reactions in the mill and thus the environment in which the particle resides (viz., the pulp chemical environment).

Subsequent to milling, the ore is conditioned. This involves adding reagents to the slurry in order to modify the surface properties of the minerals present in the ore. Reagents such as activators, collectors, frothers and depressants are all added to modify the surface properties of the various materials in the slurry, readying them for the flotation process. The collector reagents added will result in alteration of the valuable minerals surface such that it becomes hydrophobic, enabling subsequent flotation. Depressant reagents added will serve to alter the surface chemistry of the unwanted gangue such that it remains in the pulp.

The slurry then enters the bank of flotation cells where gas bubbles are passed through the pulp. Here, the hydrophobic mineral attaches to the air bubble and floats to the surface where it forms a concentrate froth that is removed. The gangue will remain in the pulp where it is removed via a tailings stream. The gas

employed in flotation separation has a pronounced effect on the outcome of the separation process since it also influences the environment in which the particle resides, that is, the pulp chemical environment (in the same vein as that stated for the grinding process above).

1.1. Scope of Research

This thesis focuses on the role of nitrogen and milling media on the pulp chemical environment and its effect on selected performance factors and their implications to froth flotation.

Firstly, a brief introduction of general flotation principles is presented, and subsequently, more detailed information regarding the pulp chemical environment and its influence on flotation behaviour is discussed. The pulp chemical environment is defined here as the water - ore - reagent medium in which the valuable particle resides during the froth flotation process. Furthermore, the role of the pulp chemical environment and its controlling factors in the various sub-processes of sulphide mineral flotation is probed. Here, specific attention is given to the minerals being treated in this study.

Finally, the merits of alteration of the pulp chemical environment are discussed and evaluated from a theoretical standpoint, which establish the research objectives.

The scope of the current research within the general flotation system is depicted in the diagram below. It follows from the analysis of the flotation system as a three tiered interacting system, with interactions between the chemical components, equipment components and operating components respectively, as first put forward by Klimpel (Klimpel, 1988).

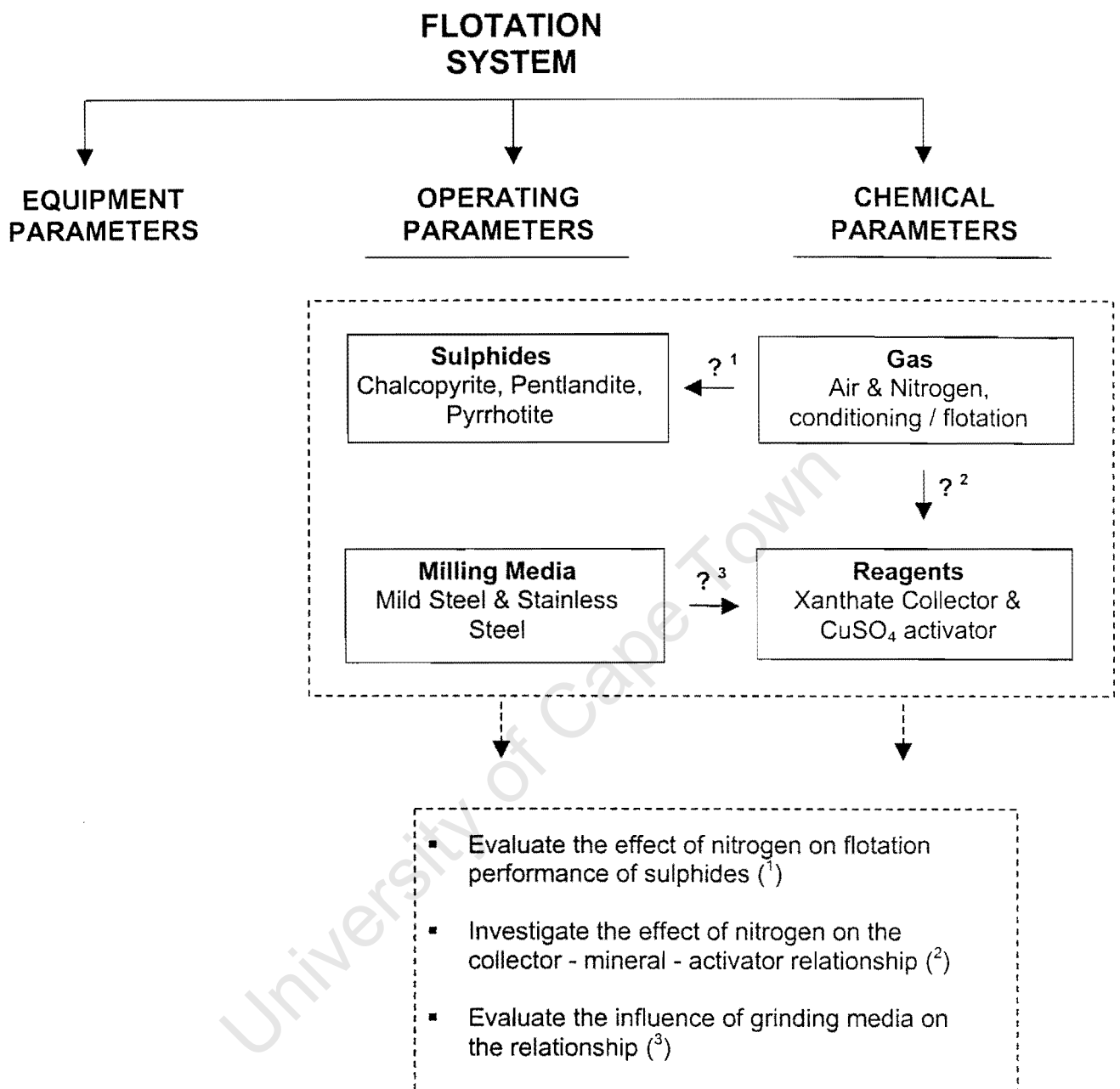


Figure 1-1: A diagrammatic representation of the current scope of research, based on Klimpel's description of a 3 tiered interacting flotation system.

2. LITERATURE REVIEW

This chapter summarises the general theory behind the flotation separation process, the basic concepts of hydrophobicity and flotability and the role of reagents in flotation. The possible effects of nitrogen on the flotation performance are discussed and previous findings are evaluated.

2.1. Hydrophobicity and Flotability

Flotation is brought about by a combination of both physical and chemical events in a flotation cell. Physically, the hydrodynamic turbulence, gas dispersion and solid suspension conditions in the cell should be such that the particle to be floated contacts with the air bubble that will subsequently remove it from the pulp. Chemically, the valuable particle's surface should be sufficiently hydrophobic such that when contact occurs, the particle must become attached and remain attached to the air bubble so as to be 'floated', and since flotation is a separation process, there is also the requirement that the unwanted gangue surface be hydrophilic in nature, and remain in the pulp to be removed as a tailing stream. Thus, hydrophobicity can be a measure of a particle's potential flotability, implying that a more hydrophobic particle is more amenable to flotation than a less hydrophobic one, from a thermodynamic standpoint.

Hydrophobicity is classically considered in terms of the thermodynamics of particle-bubble attachment, which together is the work of adhesion and cohesion, W_A and W_B respectively, leading to the derivation of the thermodynamic criterion for flotation (Laskowski, 1989).

$$\Delta G = \gamma_{LV}(\cos\theta - 1)$$

(where, ΔG = Change in Gibbs free energy, γ_{LV} = tension of the liquid-vapour interface and θ = contact angle between the liquid - vapour and liquid solid interface)

There are two relevant observations from this thermodynamic criterion;

- the thermodynamic driving force for particle-bubble attachment is greater when the contact angle (hydrophobicity) is greater.
- although hydrophobicity implies mineral flotability, it does not necessarily infer anything about the kinetic rate of the particle-bubble attachment process.

This implies that thermodynamics alone are not sufficient to ensure flotability, since both thermodynamic and kinetic considerations need to be considered. Equally important, it implies that attempts at maximising flotation performance have to concentrate both on creating the greatest thermodynamic driving force and the correct physical conditions for the flotation process. This correlates to efforts by flotation researchers on optimising the chemistry in the flotation cell and those by researchers optimising the physical cell design and auxiliary equipment and processes (viz., process control).

As regards the flotability of sulphide minerals in particular, Trahar (1984) concluded that there are at least 3 types displayed (for those that are not naturally floatable): "self-induced, sulphur induced, and collector-induced". The distinction between them, however, was made for convenience, as no information regarding how each mechanism differs from the other was known. The knowledge of the exact species responsible for the hydrophobicity (and thus flotability) of sulphide minerals has thus remained both evolving and increasing.

2.2. Reagents in Flotation

Hydrophobicity of the valuable mineral surface is a requirement for froth flotation, however, not all valuable minerals' surfaces are naturally hydrophobic and furthermore, not all unwanted gangue surfaces are naturally hydrophilic. The flotation process thus relies on the aid of chemicals to manipulate pulp chemical environment conditions to ultimately achieve the desired flotation response.

- Collectors

These compounds serve to impart hydrophobicity to the minerals surface. There are roughly 3 main classes of collectors;

- i. non polar oils
- ii. organic acids and their metal salts (anionic collectors)
 - Sulphydic collectors
 - Fatty acids
 - Alkyl sulphonates and sulphates
 - Organic sulphides
- iii. organic bases and their acid salts (cationic collectors)

The most pertinent class of collectors in sulphide flotation, are the class ii collectors, specifically the sulphydic collectors which contain the following

structural similarity; a sulphur atom double bonded to either a carbon or to a phosphorus atom, and this common constituent is further coupled to an electronegative atom, such as nitrogen, sulphur or oxygen.

The most widely used sulphydic collectors are the xanthate collectors, which are good collectors for most precious metal sulphides. Generally, they are employed in neutral to slightly alkaline mediums, as extremes on either side of the pH scale lead to problems (decomposition at low pH and problematic bubble attachment at high pH's). The following general principles have been reported with regard to xanthate collectors (SENMIN handbook);

- Increasing the chain length of the carbon chain increases absorbance.
- Increasing the chain length of the carbon chain decreases selectivity.
- Non-sulphides are not floated by xanthates (no surface adsorption).

▪ Frothers

Frothers are added to the flotation process to stabilise bubble formation in the pulp, ensure the formation of a stable froth zone, as well as to increase the rate of flotation. Frothers can be divided into categories depending on their molecular type, and are surface active non-ionic molecules. Examples of well known frothers are pine oils and PPG's (poly-propylene glycols).

▪ Depressants

The role of depressants in froth flotation is to ensure that the unwanted minerals (known as gangue) do not float. Depressants achieve this by enhancing the hydrophilic nature of the gangue's surface. The organic group of depressants are usually high molecular weight compounds, and contain strongly hydrated polar groups responsible for their depressant action. Common depressants used in the PGM industry are CMC's (carboxy methyl cellulose) and guar.

▪ Activators

Activators are added to enhance the collectors' attachment to the valuable mineral. These are usually inorganic compounds, examples of which would be copper sulphate and NaSH (sodium hydrosulphide). For complex sulphide PGM flotation, copper sulphate is usually the activator of choice and is used in this study.

2.3. Merensky Ore: Characteristics and Treatment

The Bushveld Igneous Complex in Rustenburg, South Africa, contains large reserves of platinum group metal (PGM) bearing ores. These are recovered using froth flotation as an initial means of beneficiation, and the specific method of flotation treatment varies from plant to plant depending on the nature of the ore. The PGM's occurring in this ore body are primarily associated with base metal sulphides; chalcopyrite, pentlandite and pyrrhotite, and the relative abundance of each of these and the gangue minerals differentiate between the main ore types, such as Merensky and UG-2, and their treatment methods. The present study was carried out with Merensky ore obtained from Impala Platinum mines, Rustenburg.

Merensky flotation at Impala Platinum is generally carried out in a single mill-condition-float sequence, as depicted in the following schematic (drawing based on authors observation of the circuit):

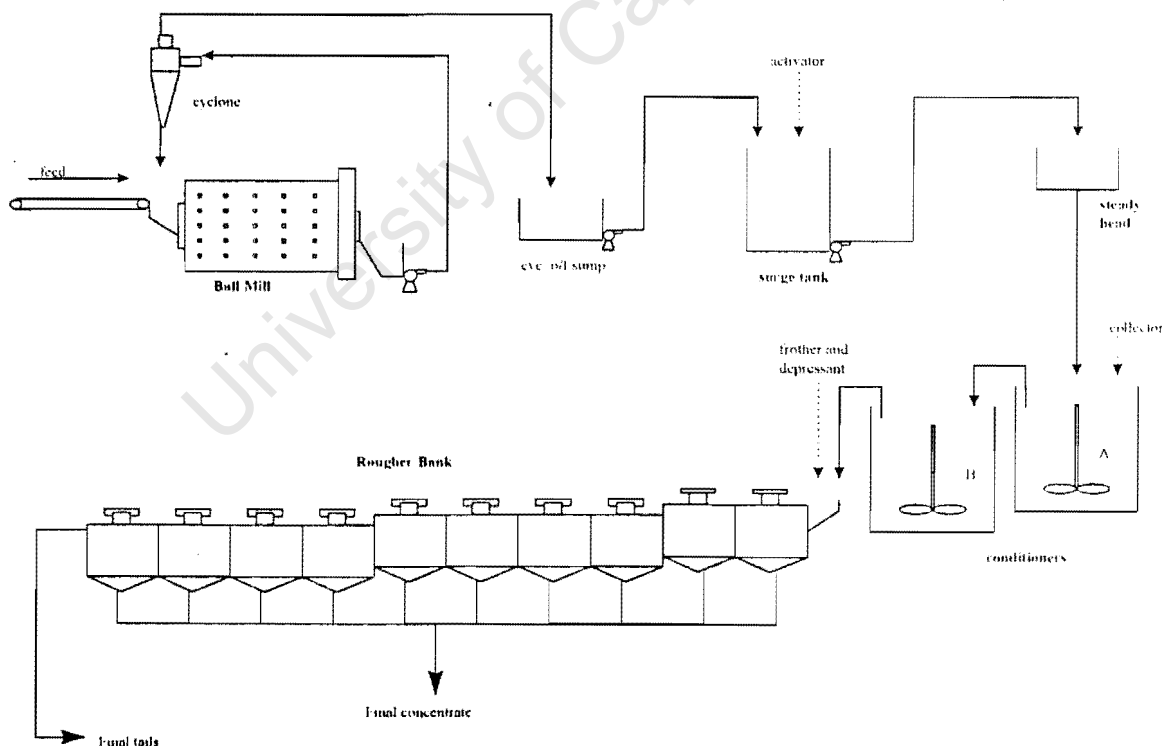


Figure 2-1: Schematic of plant flotation practice with Merensky Sulphide ore

The feed, obtained from one of 30 storage silos, is fed to the mill which grinds to a set-point of 60% passing 75 μm . The milled pulp containing about 40% solids then passes through a surge tank where it obtains its first dose of reagent, namely the copper sulphate added as activator. The 'activated' slurry then passes through the conditioners before entering the bank of flotation cells. In these conditioning tanks, the collector, frother and depressant are added. For Merensky ore, a xanthate collector mixture is used, consisting of SIBX (sodium isobutyl xanthate) together with a di-thiophosphate collector, nC4-DTP. Depressant and frother are also added. Reagents are constantly evaluated and changed due to the ever increasing need for improved plant efficiency and operation at economic optimums. The dosed feed then passes through to the head of the flotation bank. Here the ore is 'rougher floated' in 10 x 8.5 m³ rougher cells, and then scavenged and cleaned in a further 10 x 0.6 m³ flotation cells. The final concentrate and tails then proceed to subsequent smelting or tailings dams, as appropriate.

Complex sulphide ores, by definition, have (1) large quantities of pyrite (2) very fine mineral integrowth (3) minor precious and penal elements, usually (4) oxidation and alteration effects in some cases. (Barbery G, 1986). A typical Merensky feed sample for flotation in the above circuit would assay for base metals as follows:

Table 2-1: Typical Merensky base metal assay (based on actual UCT assays)

Element	Head (%)
Cu	0.06 - 0.09
Ni	0.14 - 0.22
Fe	2.4 - 4.5

Using QEM*SEM analysis, the ore can also be represented in terms of its associated sulphide minerals; chalcopyrite [CuFeS₂], pentlandite [(Ni_{4.5}Fe_{4.5})S₈] and pyrrhotite [FeS_{1.13}]. The following table shows the percentage contribution of each base metal sulphide to the total sulphide content of the ore. The total sulphide content of the ore is typically less than 2%. Additionally, there is non-sulphide nickel present in the gangue (viz., 20-30% of the total nickel occurs in the gangue, with pentlandite accounting for the remaining 70-80% of the nickel). Assays in this study are for total nickel.

Table 2-2: Typical base metal sulphide feed assay of Merensky ore

Base Metal Sulphide	% of Total Sulphides
Chalcopyrite	16
Pentlandite	32
Pyrrhotite	45

2.4. The Pulp Chemical Environment

The pulp chemical environment, as seen by a particle, constitutes all the chemical conditions (temperature, ORP, pH etc.) external to the particle and internal to the cell. Simply put, it is the flotation medium and its properties. The concept of a pulp chemical environment, and the control thereof, are central to the theme of this thesis.

The number of factors and properties required to fully describe the pulp are numerous, and to date, no attempts at identifying factors that uniquely and adequately identify pulp chemistry, and that can additionally be correlated to flotation performance, have been successful. On a more specific level, however, some studies focussing on the electrochemistry of the pulp have significantly improved our understanding of the reaction mechanisms, the environments in which they are most likely to occur, and to a limited extent, have opened the door to control of flotation performance via control of the ORP (oxidation reduction potential) and DO (dissolved oxygen) levels.

Several notations for electrochemical potential have been used. The electrochemical potential (E), oxidation reduction potential (ORP, redox, Eh), rest potential all refer to chemical reactions involving electron transfers that occur at definite associated electrical potentials. There are subtle differences, however (see Rao, Labonte and Finch (1992) for more details). The oxidation reduction potential (ORP, redox) as measured in this study are general terms. They do not imply any particular experimental condition for the system being studied except that measurements were taken. The Pt - Ag/AgCl electrode used in this study gives an indication of the mixed solution potential, as a whole, and is not indicative of the potential experienced by any mineral in particular.

The DO and ORP levels of the pulp chemical environment directly control the reaction mechanisms that govern hydrophobicity. These include the reactions

that define collector - mineral interaction, oxidation reactions and the formation of collector - activator products. In this regard, it can be seen that the DO and ORP values of the pulp ultimately affect the flotation performance, and so the question of manipulation of the DO and ORP values to enhance flotability and flotation performance arises.

The following schematic represents the principal processes related to the pulp chemistry (the four C's¹): that of *creation* of the pulp chemistry by use of reagents and other factors and the subsequent *control* of reactions according to the prevailing pulp chemical environment, both of which have a *contribution* to the resulting overall flotation performance (FP). Finally, there is the *characterisation* of the pulp chemistry with suitable measurements.

University of Cape Town

¹ Original concept of the "Four C's" by Dr. Dee Bradshaw, Minerals Processing Research Unit, University of Cape Town.

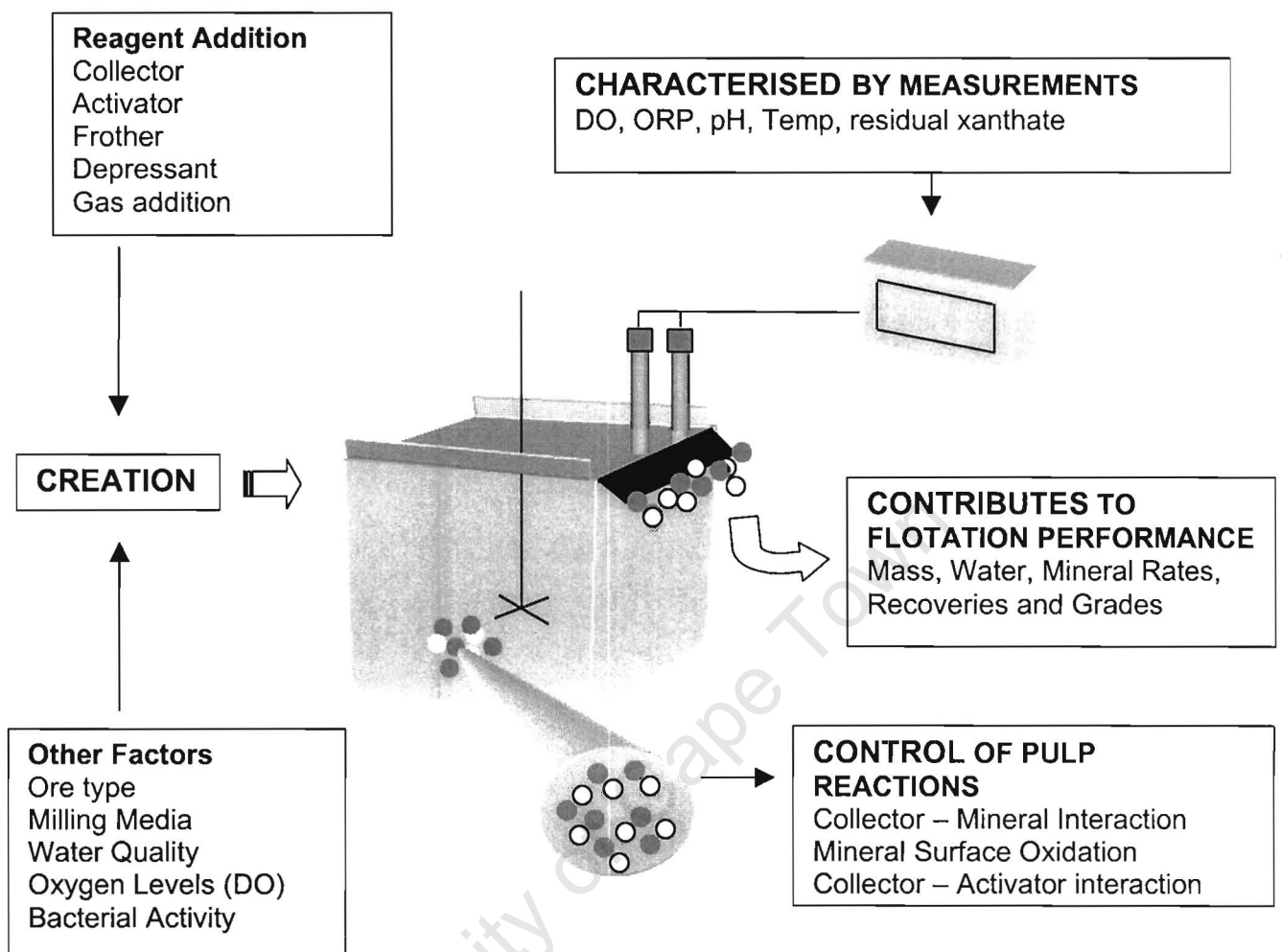


Figure 2-2: The pulp chemical environment

Manipulation of the DO and ORP levels have been carried out by a number of different methods in past research. The most common of these include the addition of reagents, changing the flotation / conditioning gas type, and changing the milling media. Classically, the addition of reagents has been carried out when attempting to control the ORP and DO values in the milling stages (with no changes to the flotation stage), and the use of different milling media and gas addition have been carried out when focus was on the flotation stage. In general, the use of reagents to manipulate DO and ORP, especially when changes to flotation conditions and reagents are under study, is avoided due to the added level of complexity in interpreting the possible interactions between the ORP modifier and the collector / activator.

2.4.1. Significance of Pulp Chemistry Measurements

Mineral processing researchers have generally demonstrated a penchant for the measurement of physical parameters in flotation, such as pulp density, flow rates, bubble and particle sizes, etc. Attention and effort in the measurement of the chemical parameters in flotation, however, has not experienced nearly as much interest up until recently. This is largely due to the fact that industry and researchers at large are beginning to recognise that the changes and improvements brought about by physical changes are nearing their plateau (Jones, 1991), and that other factors are to be considered if optimisation and improvements are to continue well into the 21st century.

In this regard, pulp chemical surveys of plants have been conducted by various researchers. The most intensive of these was conducted by Woodcock and Jones (1970) who surveyed the chemical environment of an Australian lead-zinc flotation plant by monitoring 19 parameters. Amongst the most noted and thoroughly reported parameters were the values of pH, redox potential (ORP) and oxygen concentration (DO), all of which were continuously recorded. In addition to this, xanthate residuals were assigned the next highest importance with regard to ex-situ measurements. The study was undertaken with a view to obtaining a better understanding of the pulp chemical environment, as well as to investigate any correlation of these parameters with actual flotation behaviour. Subsequent work focussing on the measurement of redox potential, dissolved oxygen levels and xanthate measurements have been carried out by a number of researchers, e.g. Jones (1991) and Adkins and Pearse (1991).

The interpretation of the flotation of sulphide minerals in terms of electrochemical processes further opened possibilities of process control for selective flotation. In this vein, vast amounts of work has been carried out on Eh measurements of sulphide minerals in flotation pulps (Nataranjan and Iwasaki (1974), Rand and Woods (1984), Labonte and Finch (1988) and Ralston (1991), to name a few).

We can conclude then, that any study that aims for a better understanding on the pulp chemical environment must, by definition, include thorough measurements of the important pulp chemical indicators relevant for that system.

2.4.1.1. Measurement of Residual Xanthate in Solution

Keller and Lewis first observed that xanthate could be measured by UV spectrometry in 1925, showing that this method of analysis has indeed been around for a long while. Schaunstein and Treiber later conducted the first well

documented set of detailed measurements of xanthate concentrations in flotation pulps in 1951, and this paved the way for Bushell and Malnarich (1956), who not only used this measurement technique on plant scale, but also used it as a control parameter for plant flotation. The method adopted in this study is thus a well known one, and it is generally accepted nowadays that the measurement of residual xanthate at the concentrations experienced in flotation pulps is best carried out by UV spectroscopy at 301 nm (Jones, 1991). The role of xanthate in flotation is still open to question, but measurement of its residual concentration by UV spectroscopy could provide useful operating information, in understanding the reactions of xanthate with other species present in the pulp.

2.4.2. Oxygen in Sulphide Flotation

The role of oxygen in sulphide mineral flotation has been the focus of much research in recent years, principally due to its interactions with flotation reagents as well as the mineral surface (Woodcock and Jones (1970), Houot and Duhamet (1990), Rao and Finch (1990), Kelebek (1993), Clarke et. al. (1995)). Its presence in most flotation plants is simply as a consequence of pulp being in contact with the atmosphere and the utilisation of air as a flotation gas. It is cheap and readily available, and is a requirement for the flotation of most sulphides since it allows the reaction between sulphides and xanthate to occur (Woodcock and Jones, 1970). In many cases, flotation with pure oxygen has led to improvements in flotation performance (Tipman et.al., 1976 and Houot and Duhamet, 1989). Other than the classical function of interaction with the collector, oxygen also affects the surface reactions occurring on the mineral, as well as the oxidation reactions occurring with the cationic species present in the pulp (e.g., Cu^{2+} , Fe^{2+} , Fe^{3+}).

Oxygen enters the solution by dissolution from air bubbles, either by force fed air, or by turbulent agitation and pumping under the action of the impeller. In addition, equilibrium levels of dissolved oxygen are initially present in the water. Conversely, oxygen is removed from the system by reactions with sulphide minerals, ions in solution and reagents. These competing processes eventually reach equilibrium within the pulp, and gives rise to a measurable level of saturation of the pulp. This level of oxygen saturation can be used together with the value of the redox potential (Eh) to glean useful information regarding the possible reactions occurring in the pulp. The role of oxygen in electrochemical studies is thus linked primarily to the redox and dissolution/oxidation reactions occurring in the pulp. Researchers have also attempted (sometimes successfully)

to correlate other parameters like pH and Eh with oxygen saturation levels of the pulp (Woodcock and Jones, 1970), although stating at the same time that in many systems, oxygen levels can vary without any apparent effect on the Eh.

2.4.3. Influence of Oxygen on the Mineral Surface

Oxygen has a strong effect on the condition of the sulphide mineral's surface. It is utilised both in the processes that positively render the surface hydrophobic, and at the same time, negatively in the oxidation and formation of hydroxy species that can render the same surface hydrophilic.

Surface oxidation products of sulphide minerals consist mainly of metal hydroxides and sulphur-oxy species, which occur either as layers on the particle, or if conditions are appropriate, precipitate directly from solution (Clarke et al, 1995). The oxidation products of the sulphide minerals of interest in this investigation, for basic solutions, can be found below (Woods, 1984).

Table 2-3: Oxidation products of sulphide minerals (Woods, 1984)

Mineral	Oxide	Sulphide	Major Sulphur	Minor Sulphur
Fe_{1-x}S	$\text{Fe}(\text{OH})_3$	-	S	SO_4^{2-}
CuFeS_2	$\text{Fe}(\text{OH})_3$	CuS	S	-
$(\text{Fe},\text{Ni})_9\text{S}_8$	$\text{Fe}(\text{OH})_3$	NiS	S	SO_4^{2-}

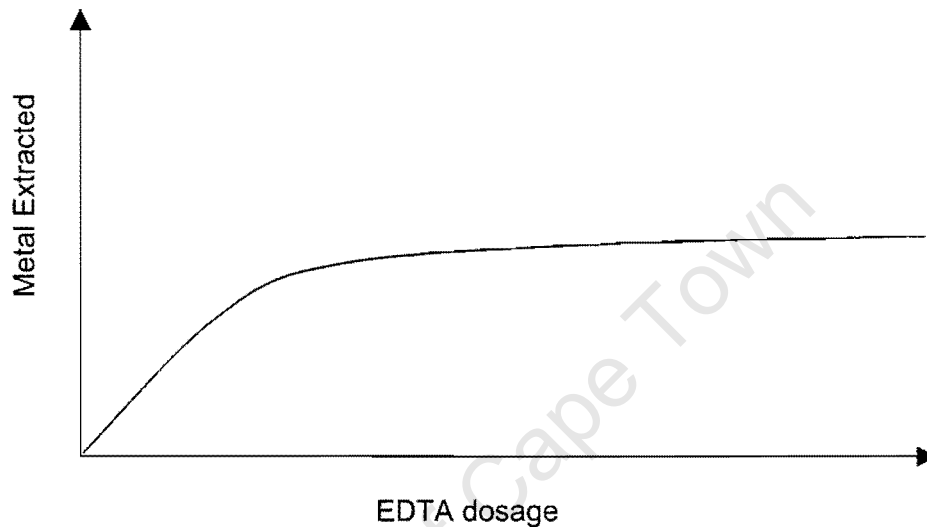
NI= not identified

Recent studies (Rumball, 1994, Clarke, 1995) have attempted to monitor and measure the extent of oxidation on sulphide minerals using EDTA (ethylene diamine tetra acetic acid), a strong complexant. EDTA is known to 'clean' the surfaces and render them free of metal hydroxides. The table below shows that the EDTA complexes with the metal hydroxide but not with the metal sulphide.

Table 2-4: Log K values for various Metal Ion - EDTA complexes and metal sulphides (Clark, 1997)

Metal Ion	Log K value		
	Metal Ion - EDTA	Metal Sulphide	Metal Hydroxide
Cu (II)	18.8	22.1	6.86
Fe (II)	14.3	18.0	12.9
Fe (III)	25.1	-	17.5

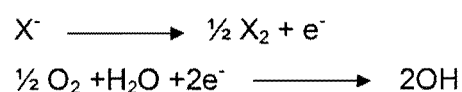
In theory, this implies that the extraction of surface hydroxides will be initially be proportional to the dosage of EDTA. As there is a finite amount of metal present as hydroxides on the surface, the rate of extraction will then slow and the amount of metal extracted will eventually level out at some plateau, since the metal cannot be extracted from the sulphide metal itself. This is graphically depicted below.



Success has been limited to pure mineral studies, and is generally qualitative with regard to results in complex systems. If this technique can be applied to a complex sulphide ore like Merensky used in this study, it will aid in the understanding of oxidation of the ore in circuit, as well as provide useful information regarding the specific role of nitrogen in its ability to hinder oxidation of the mineral's surface.

2.4.4. Influence of Oxygen on Collector Oxidation

An important derivative formed as a result of xanthate oxidation is dixanthogen, which may form at the mineral surface via the following redox reaction (occurring at between 200-220 mV S.H.E).



Noticeably, oxygen is needed here as an electron donor, and inhibiting oxygen levels directly restricts the formation of the dithiolate product. Collector - mineral studies show this (dithiolate) to be the responsible species for flotation of certain minerals, for example pyrrhotite (Allison et al, 1972). Recent developments,

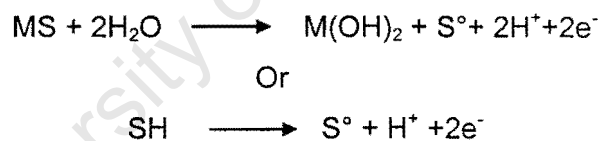
however, indicate differences for certain minerals and under certain conditions (Bradshaw et. al., 1999). The role of dixanthogen thus remains controversial.

2.4.5. Collector – Mineral Interactions

The mineral – collector interaction in sulphide systems is thought to take place by an electrochemical mechanism during which anodic processes involving the oxidation of mineral and collector are coupled with the cathodic reduction of oxygen (Trahar, 1984). It follows then that oxygen is necessary for interaction of the mineral with collector. Past research has shown clearly that when no oxygen is present, sulphide minerals do not interact with xanthate, and that a subsequent small increase in oxygen concentration leads to both improved flotation and increased rate of interaction of mineral and collector (Yuan et al, 1996).

2.4.5.1. Chalcopyrite – Xanthate Interaction

Chalcopyrite shows collectorless flotation, except under conditions where it has been dry milled (Kocabag, 1994). This suggests that if there is no galvanic interaction or corrosion effects, then no collectorless flotation will occur. Collectorless flotation of chalcopyrite is attributed to S° formation on the surface of chalcopyrite (formed by oxidation of the mineral).



The initial chemisorption of xanthate on chalcopyrite is possibly as follows



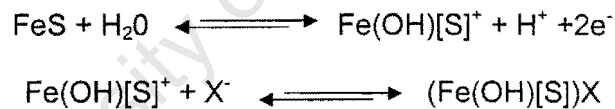
As with other sulphide minerals, chalcopyrite requires initial oxidation for flotation. Klymowsky and Salman (1970) showed that collector adsorption on chalcopyrite increased as concentration of oxygen in the pulp was increased. This increase however, does not necessarily imply increased flotability, since excessive oxidation is also detrimental to sulphide flotation. Both Allison (1972) and Persson (1993) confirmed the reaction product of chalcopyrite in a xanthate solution to be dixanthogen, at a rest potential of 0.14 V. The equilibrium potential of the xanthate/dixanthogen couple in this instance is reported as 0.13 V (at their respective pH and concentrations of potassium ethyl xanthate). This agreed with the observed surface species.

2.4.5.2. Pyrrhotite – Xanthate interaction

The xanthate - pyrrhotite interaction is known to follow a charge transfer mechanism (each reaction occurring at a specific potential) resulting in a chemisorbed film of xanthate at the mineral surface. During the charge transfer mechanism, the electrons from xanthate are transferred to oxygen dissolved in water. As a result, this reaction is suppressed if the dissolved oxygen in the water has been removed by the addition of nitrogen (to < 1 ppm). This is also observed with pyrite and chalcopyrite (i.e. lowered chalcopyrite recoveries found by some researchers, e.g. Kelebek, 1993).

Chang et.al. (1954) found high pyrrhotite recovery at pH < 4. The adsorption of Xanthate must follow a different mechanism at pH < 4 (possibly chemisorption of xanthate at Fe²⁺ sites produced in acidic pH) since the Fe is present as Fe²⁺, not Fe(OH)⁺. Alternatively, this finding could be as a result of surface cleaning via removal of the hydrophilic hydroxides that decompose at low pH.

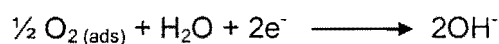
Many plants achieve pyrrhotite flotation even up to pH 9. This could be explained by Hodgeson & Agar's adsorption mechanism where xanthate is adsorbed on pyrrhotite through coulombic interaction with Fe cationic III sites generated via oxidation of the mineral surface.



This suggests that oxygen is essential for xanthate - pyrrhotite interaction (i.e. the mechanism relies on oxygen to act as electron acceptor) and that reducing oxygen activity by nitrogen addition could affect the flotation of pyrrhotite. The mechanism still allows for the subsequent possibility of residual xanthate on the surface to further oxidise to dixanthogen through oxygen reduction at the pyrrhotite surface, and is therefore not contradictory to research concluding that dixanthogen is the major hydrophobic species responsible for pyrrhotite flotation.



Accompanying this half reaction, is the reduction of adsorbed oxygen



With an increase in pH above 9, however, the pyrrhotite recovery drops. This is explained by the formation of $\text{Fe}(\text{OH})_3$ at this pH via oxidation of $\text{Fe}(\text{OH})_2$ or a high concentration of OH^- ions hindering the adsorption of xanthate (Barsky relationship, where $[\text{X}^-]/[\text{OH}^-] = \text{constant}$).

2.4.5.3. Pentlandite – Xanthate Interaction

Oxidation of pentlandite results in the same oxide, major sulphur and minor sulphur as for pyrrhotite.

The xanthate – pentlandite interaction is thought to occur by initial chemical adsorption of xanthate onto the pentlandite surface, followed by oxidation to dixanthogen (Hodgson and Agar, 1989). Surface studies by XPS (X-Ray photoelectron spectroscopy) and ATR (Attenuated total reflectance) FTIR (Fourier-transform infrared spectroscopy) have confirmed that the major species on the pentlandite surface after xanthate addition is dixanthogen (Valli and Person, 1994 and Xu and Finch, 1996).

It may be likely that the species responsible for flotation is similar to that for pyrrhotite; i.e. a mixed film of xanthate and dixanthogen, however, Kelebek (1993) has reported pentlandite flotation even under oxygen free conditions (where dixanthogen formation is unlikely). This has been attributed to pentlandites' high catalytic activity allowing it to develop hydrophobicity even under oxygen deficient conditions.

2.4.6. Galvanic Interactions

When two or more sulphide minerals are in contact, the differences in their electrochemical reactivities causes a 'galvanic interaction' to occur. During this interaction, the mineral with the higher electrochemical reactivity draws electrons from the mineral with the lower electrochemical reactivity, and thus reduces it. In practice, the rest potential of the mineral is an indicator of its electrochemical reactivity; the higher the rest potential, the nobler the mineral.

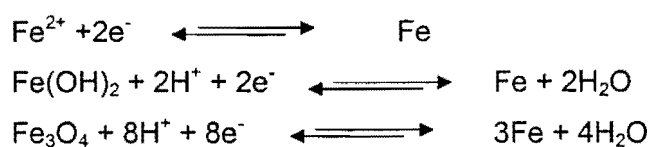
The two requirements essential for the occurrence of galvanic interaction are therefore; (1) physical contact between the different sulphide minerals (in slurries, milling, or in locked particles) and (2) the presence of oxygen for the cathodic reduction reaction (and subsequent anodic oxidation of the sulphide mineral).

2.5. The Mill Environment: Reactions

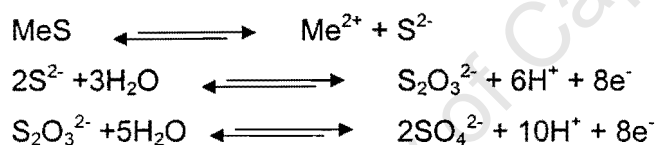
The first stage in the preparation of ore for flotation involves liberation of the valuable mineral particles from the gangue by size reduction. This is achieved by

grinding the ore in a mill charged with either a conventional, autogenous or semi-autogenous charge. The nature of the grinding environment is crucial to the subsequent flotation response, since it also represents the particle's first exposure to the outside pulp environment and its complex chemistry. Examples of such reactions from the mineral-mineral, mineral-collector and mineral-media interactions occurring are; "dissolution of oxidised species, release of metal ions into the pulp solution, precipitation, adsorption of the reaction products onto mineral surface" (Subrahmanyam, 1992).

The reducing environment in a conventional mill may be due to any of the following reactions (Subrahmanyam and Forssberg; 1993, 1993).

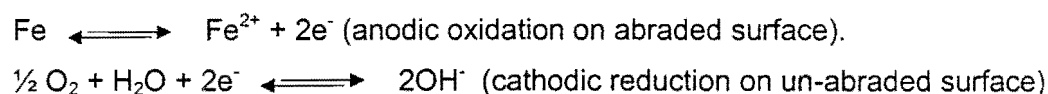


similarly, the oxidising environment in an autogenous mill is due to:

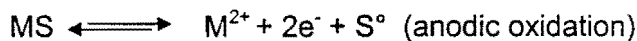


In summary, for conventional milling (reducing environment): The reactions that occur are corrosion reactions and the mineral-media interaction. Since the rest potential of sulphides is greater than that of the media (Fe), the media gets anodically oxidised, liberating Fe into solution. These Fe species (and any other species present like Cu^{2+} , Pb^{2+} , Zn^{2+}) may form metal hydroxy complexes which impair natural flotability and interfere with collector adsorption, as we shall see mechanistically depicted below. Other than the above authors, other studies on the influence of grinding on the flotability of sulphides in terms of galvanic interactions (Adam and Iwasaki, 1984 and others) generally agree that the media-mineral interaction leads to oxy-hydroxide coatings on the noble minerals thus affecting their flotability. They site the following reactions as occurring on the media and mineral surface;

(a) on media surface:



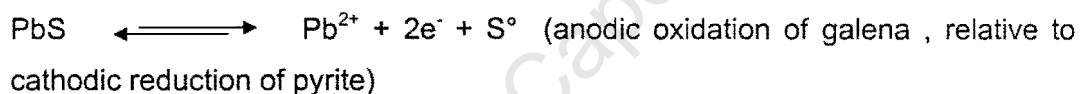
(b) mineral surface (say metal sulphide, MS)



the hydroxide ion (OH^-) released during the cathodic reduction of oxygen may react with metal ions to form metal hydroxy complexes. i.e.



(c) In a media-mineral galvanic couple, cathodic reduction of oxygen occurs on the mineral surface (highest rest potential) while the media undergoes anodic oxidation. When other minerals are present (i.e. for complex sulphides, pyrite, chalcopyrite, galena), then the minerals with the lowest rest potential are oxidised with respect to the minerals with the highest rest potential (pyrite, in this example).



In a complex sulphide mineral system like Merensky ore, under appropriate conditions, multi-electrode galvanic cells can form. For example, in the Fe-Cu-Ni (pyrrhotite, chalcopyrite, pentlandite) system, the noblest mineral in the series will act as the cathode and the grinding media as the anode. The other minerals will display relative anodic/cathodic behaviour, based on their rest potentials relative to each other. In this instance, it becomes apparent that some minerals can be "cathodically protected" from oxidation, and are subsequently less/not coated with the hydroxyl ions formed via iron dissolution (anodic oxidation) of the media's surface. The low concentration of sulphides, however, decrease the likelihood of the protection mechanism occurring on a large scale.

It is important to note that in all the reactions described above, oxygen once again plays a vital role, and that the rate of oxygen reduction is directly related to the rate of hydroxyl ion formation which is seen to be detrimental to the flotability of certain sulphide minerals (Nakazawa and Iwasaki, 1985, Rao and Finch, 1991).

2.6. Flotation in Oxygen Deficient Environments

2.6.1. Methods of Oxygen Removal and their Implications

Oxygen removal during flotation testwork has been carried out by a number of researchers, both in flotation studies as well as more fundamental studies on collector adsorption (for example, Chang et.al., 1954, Nakazawa and Iwasaki, 1985, Martin et.al., 1989, Rao and Finch, 1991, Rybas, et.al., 1993, Cheng et.al., 1994, etc.). It can be achieved in various ways depending on the scale of operation and the level of complexity one is prepared to introduce into the problem. Historically, past researchers have most often used the addition of an inert gas, typically nitrogen, to purge the system of oxygen (Forssberg, 1993 & 1993, Kelebek, 1993 and Rao et.al., 1995). Others have investigated the use of mild steel milling (conventional milling) relative to stainless steel milling (semi-autogenous milling), and noted that mild steel results in a decrease in the ORP and DO levels, an effect similar to that of nitrogen, but with the added complexity of also drastically altering the pulp chemistry of the system (Forssberg, 1993 & 1993). The intent with regard to milling media in those instances was not primarily to lower the DO and ORP, as is the case in this study.

In summary, for control of pulp conditions, a number of different methods of oxygen removal can be employed (cf. 1.5);

- use of reagents (oxygen consuming)
- use of reducing milling media (mild steel)
- use of gases (nitrogen/argon)

In practice, the use of reagents has been avoided, as it constitutes a level of added difficulty to the problem by introducing a compound whose mechanistic role under the test conditions is not always fully understood. Researchers thus far have therefore mainly used variations in milling media and gas type to control the level of oxygen in the system as these represent easy and readily available methodologies. Additionally, they lend themselves well to practice in industry.

2.6.1.1. Prior to Flotation

Here, oxygen removal can be achieved by either milling with mild steel media, adding nitrogen as a conditioning gas, or adding nitrogen directly to the mill. In all instances, the outcome is a pulp with very low oxygen activity sent to the froth flotation stage. Here, the actual point of gas addition controls the collector-mineral interaction, since it affects the pulp chemistry and the environment that the

mineral 'sees'. If nitrogen gas is added to the mill, for example, and collector is subsequently added, the low oxygen activity of the pulp hinders the collector oxidation process (i.e. formation of dithiolate). If the pulp is allowed to equilibrate and once again saturates with oxygen, clearly the issue is no longer as important, but if nitrogen conditioning and/or nitrogen flotation is to follow, then the time scale of 'oxidation' events becomes critical to the success/failure of the flotation process.

2.6.1.2. During Flotation

Here, nitrogen or argon gas is added during the flotation stage. In this instance, the collector has been added prior to contact with the gas (in the conditioning stage), and if no other pre-conditioning was effected, the mineral surface should by this stage be amenable to flotation. Addition of nitrogen/argon, at this point in the process, has historically been to stop galvanic interactions and benefit from any outcome of this (for example, in pyrite -sphalerite separation). It must be noted, in this instance, that the final outcome is equally dependant on any gas addition during the conditioning step prior to this.

2.6.2. The Effects of Nitrogen Gas and Reducing Milling Media on Pulp Chemical Conditions

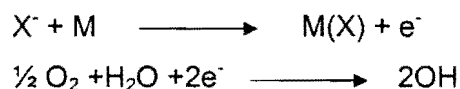
The role of nitrogen in the flotation of sulphide minerals has two areas of interest. Firstly, it lowers the pulp potential and activity of oxygen in the system. This may influence the flotation result by affecting the extent of oxidation of sulphide minerals taking electrochemical considerations into account. Secondly, oxygen plays a role in collector adsorption and in the formation of dithiolate at the mineral's surface.

The principle of reduced oxidation (via employment of nitrogen gas) has also been used in other flotation processes, viz. molybdenite flotation from copper / molybdenum bulk concentrates, where the oxidation of an expensive secondary reagent leads to undesirable losses. In this instance, a process employing nitrogen has been successfully patented (British patent No. 1307320, 1972).

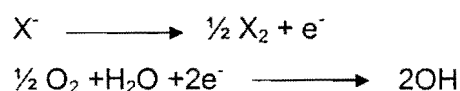
Sandoval et.al. (1989) reported that the use of nitrogen proved useful in pyrite-sphalerite separation, for the selective flotation of pyrite ahead of sphalerite. Rao and Martin also observe the promotion of pyrite flotation by nitrogen. They attribute this to the weakening of the galvanic interaction between pyrite and sphalerite. This conclusion is based on electrochemical considerations which partly govern flotation; that is, the interaction between the collector and mineral

correspond to a specific potential. For a system with xanthate as collector, the redox reactions occurring are as follows:

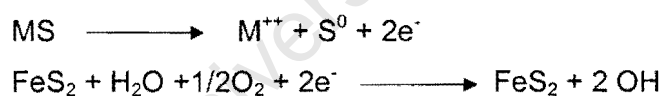
1. Surface adsorption of xanthate occurring between 60 and 70 mV E_h (or -162 and -152 mV $E_{Ag/AgCl}$)²



2. Oxidation of Xanthate collector at surface occurring between 200-220 mV E_h (or -22 and -2 mV $E_{Ag/AgCl}$)



As indicated, oxygen is needed in both redox reactions as an electron acceptor. For pyrite, it is generally thought that the dithiolate is the required species for imparting hydrophobicity to the surface, and so, control of the potential (and/or oxygen levels) to levels below 200 mV (E_h) and greater than 60 mV (E_h) could hinder pyrite flotation. It is important to note, however, that in practice, the presence of other sulphide minerals in contact with the pyrite lead to "galvanic interactions". In a complex sulphide mineral, pyrite is often the most cathodic mineral present and this results in the formation of a hydroxide rich layer on the minerals surface.



It is important to note at this point, that for the sulphide Merensky ore under study, only trace amounts of pyrite occur, and pyrrhotite takes the role as most cathodic mineral in the ore under consideration. Any views expressed by past researchers with regard to the electrochemistry of the most cathodic mineral can thus generally be extended to pyrrhotite in this instance.

² Literature value for potential, E_h , given relative to standard hydrogen electrode (SHE), has been converted to a standard Pt - Ag/AgCl electrode potential, $E_{Ag/AgCl}$, by adding 0.222 V (Rao, 1992).

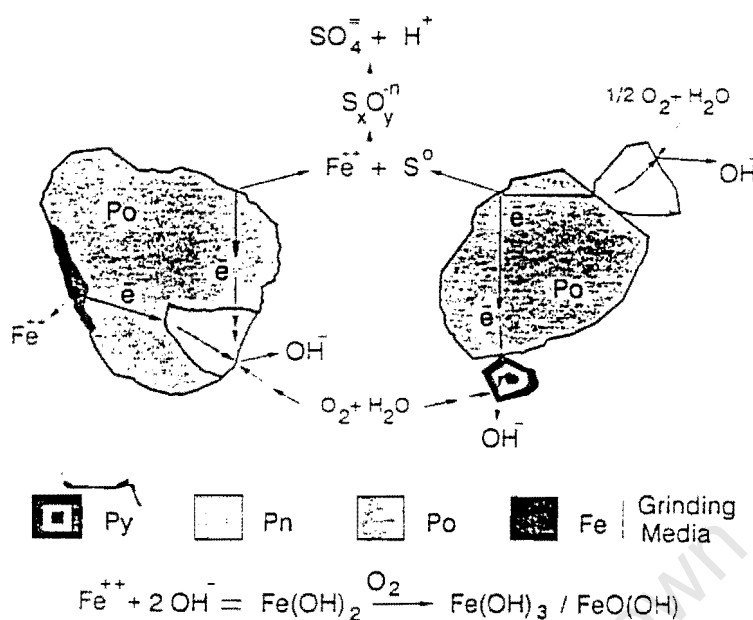
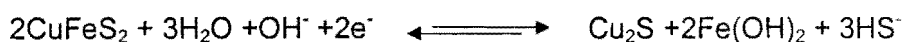


Figure 2-3: Electrochemical interactions and the surface reactions involved in preferential oxidation of pyrrhotite and grinding media (Source: Kelebek, 1993)

Once again, the role of oxygen in galvanic interactions is noted, and purging of oxygen from the system can lead to the hindering of galvanic interactions. In conclusion, promotion of pyrite mineral flotation with the use of nitrogen has been attributed to 1). weakening of galvanic coupling 2). prevention of formation of OH^- ions, and 3). lower levels of OH^- which competes with X^- for adsorption (Barsky relationship).

Instances of apparent disparity have been found in the literature, where the use of nitrogen in pyrite flotation leads to depression of the mineral (Rao and Finch, 1987). These can be explained when the point of nitrogen addition has been considered (during flotation or during conditioning), as the specific mechanism of xanthate adsorption depends largely on the nature of the pulp chemistry at the time of collector addition. That is, if nitrogen is added immediately after grinding and before collector addition, then the formation of a hydrophobic film on the minerals surface is severely restricted, however, if nitrogen is added after the mineral has interacted with collector, the collector-mineral interactions dependence on oxygen has been met, and the nitrogen serves to hinder other side-reactions / galvanic interactions. Note that although pyrite is the mineral under consideration here, the issues highlighted apply to any sulphide mineral having similar chemical and electrochemical requirements for flotation.

With regard to chalcopyrite and pentlandite, Kelebek noted that when nitrogen milling and flotation were employed, there was a large decrease in flotation recovery of copper, the order of flotability changing to Pentlandite > Chalcopyrite > Pyrrhotite. The authors have suggested the possibility that the lowered activity of oxygen prevents xanthate adsorption and thus lowered hydrophobicity of the chalcopyrite particle. Furthermore, there is a suggestion that chalcopyrite can undergo a cathodic decomposition under oxygen free conditions. The reaction is proposed as;



The iron hydroxide formed could explain the poor flotability. The observation is, however, that chalcopyrite retains its relatively strong hydrophobicity upon aeration of the pulp.

Study of the experimental procedure used by Kelebek shows that nitrogen was added both in the milling and flotation stages, and it is likely that the lack of oxygen restricts the formation of a hydrophobic surface species via collector-mineral interaction. This is thought to be the more rational of the proposed explanations. In this instance however, pentlandite recoveries were unchanged. Once again, reference to pentlandite's ability to render its surface hydrophobic even under oxygen deficient conditions (see c.f. 2.4.5.3) was proposed to explain this, however, it is felt that the hydrophobic entity required for pentlandite flotation may well be the metal xanthate alone, and not necessarily a combination with the dithiolate. New breakthroughs in this area may shed light on this observation in future.

Rao and Finch (1991) studied the adsorption behaviour of xanthate on pyrrhotite in the presence of nitrogen. Xanthate uptake was lowered in the presence of nitrogen, and while xanthate uptake still occurred, no dixanthogen was formed on the mineral surface (at pH 6). At pH 8.4, however, there was no decrease in xanthate uptake. If xanthate was chemisorbed, uptake should be lower at higher pH values due to hindrance by the OH^- ion (Barsky relationship). This suggested that the mechanism was not a charge transfer mechanism.

Their results also showed that xanthate-dixanthogen uptake was greater in air than in nitrogen when no cationic species was present in the water, and that uptake still occurred in the presence of nitrogen probably due to superficial oxidation of pyrrhotite. This is likely, since pyrrhotite is known to oxidise very

rapidly i.e. Fe^{++} ions form and interact with H_2O to give $\text{Fe}(\text{OH})^+$ species.

Since the concentration of $\text{Fe}(\text{OH})^+$ is maximum at pH 8.5, their explanation was that these cationic species served to electrostatically attract the anionic xanthate, explaining why there was no decrease in xanthate uptake at pH 8.4.

It is interesting to note, however, that in the presence of nitrogen, no dixanthogen was formed at the mineral surface, but only in solution. In this instance, the presence of an oxidising ion (like Cu^{++}) was used to explain this difference. The results seem to justify this, since no dixanthogen was found in solution under similar conditions when a non-oxidising ion (like Ni^{++} was used). The above findings are directly relevant to any sound interpretation of the results since it shows clearly the effect of other ions in solution, and how their presence directly affects the nature and entity of the hydrophobic species present.

More directly pertinent to this study, are the results of Rybas et al (1993), who used nitrogen in the flotation of a copper-nickel ore. Here, they report depression of pyrrhotite on an industrial scale by the use of nitrogen (together with an organic depressant) in flotation, and exploitation of this depression by selective recovery of pyrrhotite at a later stage using flotation at low pH of 2.2. Their specific findings are an increase in nickel grade in the first concentrate (7-8%) at constant recovery, and reduction of SO_2 emission by 30-50 % by better separation of the sulphur containing pyrrhotite material. This provides an interesting kickback from an ecological point of view, and highlights another advantage of employing "clean" float technology to the flotation process.

X.-M Yuan and co-workers (1996) recently conducted a study investigating the manipulation of pulp potential on the selectivity control of a complex sulphide ore (Cu/Zn). The pulp potential was manipulated by the use of gases having different oxygen contents; pure nitrogen, 5% oxygen and air. The tests were carried out using both reducing (mild steel) and autogenous (oxidising) milling, and the gases were employed in a 'pre-conditioning' stage, as well as a 'flotation' stage. In this regard, it is important to note that gas pre-conditioning was done prior to any reagent addition, and subsequent stepwise gas-conditioning and reagent addition took place simultaneously.

They concluded that the milling had the most dominant effect on the copper recovery. At the same time, however, this effect was linked to the type of preconditioning. Stainless steel results showed no dependence of copper recovery on flotation or preconditioning gas type, while mild steel milling showed dependence on pre-conditioning and flotation gases.

Once again, these results are generally in keeping with those observed for copper recoveries as reported elsewhere. In this instance, no nitrogen addition was employed during milling, as this is the only time that decreases in copper recoveries have been observed in past research. The low recoveries with mild steel are linked to the low oxygen activity of the pulp, further exaggerated by the use of nitrogen prior to any addition of collector.

In summary, we can conclude that ascertaining the effect of oxygen removal for complex sulphide ores is not trivial, and the result depends to a large extent on the exact method employed as well as the ore type being processed.

In order to evaluate the effect of nitrogen on the processing of Merensky ore from Impala Platinum mines, the following research objectives were addressed.

2.7. Research Objectives

As outlined in section 2.6.1 above, the addition of nitrogen is a means of manipulating the DO and ORP levels of the pulp chemical environment. In section 2.6.2 above we also noted that oxygen removal by nitrogen addition could lead to a variety of pulp chemical reaction scenarios that could either benefit or hinder flotation performance depending on the type of ore being treated. The overall objective of this research is as follows:

"To establish the *influence of nitrogen addition* on the flotation performance of *sulphide PGM bearing ores*, and to develop an understanding of the mechanisms involved."

More specifically, the research objectives are as follows:

1. To investigate the effect of nitrogen on the metallurgical flotation performance of a complex sulphide ore, viz.:

- To establish what effect the use of nitrogen has on the batch flotation performance as measured by mineral recoveries and grades (Cu, Ni, Fe) and on the froth characteristics represented by overall mass and water recoveries.

- To ascertain the effect of nitrogen addition at different points in the batch flotation process (viz., the use of nitrogen in conditioning vs. the use of nitrogen as flotation gas, and combinations thereof).
 - To confirm whether the effect of nitrogen addition is consistent under different operating conditions (viz., are the observations consistent for both mild steel and stainless steel milling media).
- 2. To develop an understanding of the mechanisms of nitrogen addition on the relevant sub processes and interactions in froth flotation using complementary investigative studies:**

2.1. To evaluate the role of nitrogen on the pulp chemical environment, viz.;

- Establishing the effect of nitrogen on the pulp chemistry as described by profiles of DO, ORP, pH and temperature measured during the flotation tests.
- To establish whether it is merely the lowering of ORP and DO by the removal of oxygen that produces the observed effect ? (This can be tested by noting that the use of mild steel milling media would be equivalent to the use of stainless steel milling media plus nitrogen addition with the same ORP and DO levels being achieved).
- To establish whether nitrogen addition and the subsequent lower ORP hinders collector - mineral interaction or dixanthogen formation on any of the minerals in the flotation stage, and whether this subsequently affects mineral flotability as measured by the resulting flotation performance.

2.2. To evaluate the influence of nitrogen on mineral surface oxidation, viz.;

- To establish whether nitrogen reduces surface oxidation and in doing so causes enhanced mineral flotability of certain minerals.
- To establish whether this reduced surface oxidation (if any), is measurable.
- To establish whether the extent of surface oxidation is affected by the use of different milling media (mild steel vs. stainless steel).

2.3. *To evaluate the influence of nitrogen on the collector – mineral interaction, and additionally, evaluate this influence in the presence of activator (CuSO₄) and ferrous iron (as present after mild steel milling), viz.;*

- To establish whether the collector - mineral interaction has proceeded to completion during conditioning, or is ongoing during flotation.
- To establish whether nitrogen affects the CuSO₄ – xanthate – mineral interaction.
- To establish whether iron abrasion during mild steel milling affects the role of nitrogen in the pulp, and to identify the secondary effects (viz., froth stability).

3. BATCH FLOTATION

This phase of work studied the effect of nitrogen addition (after reagent addition), used either as a conditioning gas and / or a flotation gas. The tests were carried out using pulp prepared by both mild steel and stainless steel media in the milling stage.

The specific objectives of this phase of work were;

- i. To establish what effect the use of nitrogen has on the batch flotation performance as measured by mineral recoveries and grades (Cu, Ni, Fe) and overall mass and water recoveries.
- ii. To ascertain the effect of nitrogen addition at different points in the batch flotation process (viz., the use of nitrogen in conditioning vs. the use of nitrogen as flotation gas, and combinations thereof).
- iii. To confirm whether the effect of nitrogen addition is consistent under different operating conditions (viz., are the observations consistent for both mild steel and stainless steel milling media).
- iv. To observe nitrogen's effect on the pulp chemistry as described by profiles of DO, ORP, pH and temperature measured during the flotation tests.

3.1. Experimental Details

3.1.1. Ore Collection and Sampling

A Merensky ore sample was taken as a belt cut at Impala Platinum mines, Rustenburg. The 250 kg sample of large, fist sized pieces of ore was crushed, split into 1kg samples, sealed under nitrogen and stored frozen in the UCT flotation laboratory. Exposure time to the atmosphere was controlled and the ore was under a nitrogen blanket where possible.

3.1.2. Flotation Apparatus

3.1.2.1. Mill

The ore was milled in a Sala laboratory stainless steel rod mill. The diameter of the mill was 300mm and the diameter of the rods were 25mm. The mill charge was 20 rods of either mild steel or stainless steel charge, as dictated by test conditions.

3.1.2.2. Flotation Cell

The flotation cell used in the batch flotation testwork was a modified 3 – litre Leeds laboratory cell. The cell was fitted with a variable speed drive and the pulp level was controlled with a constant head device so as to give a constant froth height of 2 cm. A pictorial of the customised flotation setup can be seen in Figure 3-1 below

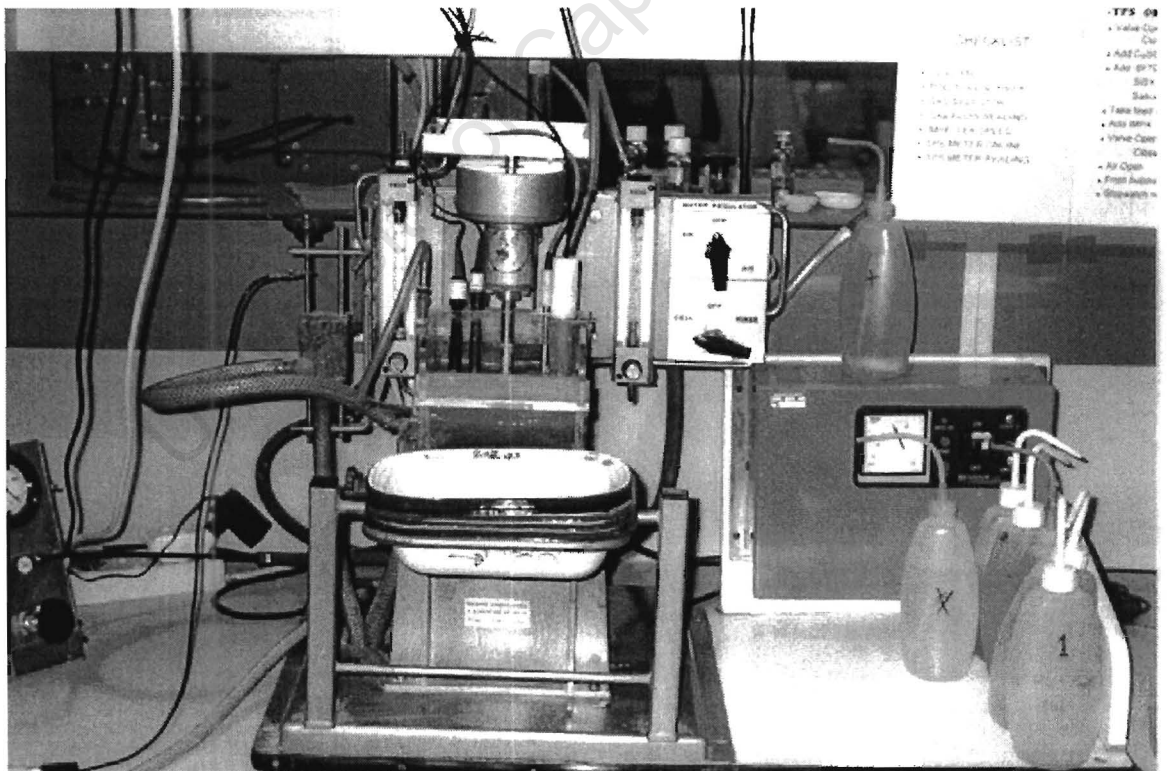


Figure 3-1: Pictorial of batch flotation cell setup

3.1.2.3. TPS Meter

A TPS meter was used to monitor the temperature, pH, oxidation – reduction potential (ORP), and dissolved oxygen (DO) levels in the pulp. The flotation cell was customised to accommodate the probes and the position of each probe was fixed for the duration of the testwork. The temperature was measured with a standard thermocouple. The pH was measured with a GLASS combination electrode. ORP was measured using a combination platinum silver / silver chloride electrode (Pt - Ag/AgCl). DO was measured using a YSI probe. A pictorial of the TPS meter in operation can be seen in below.

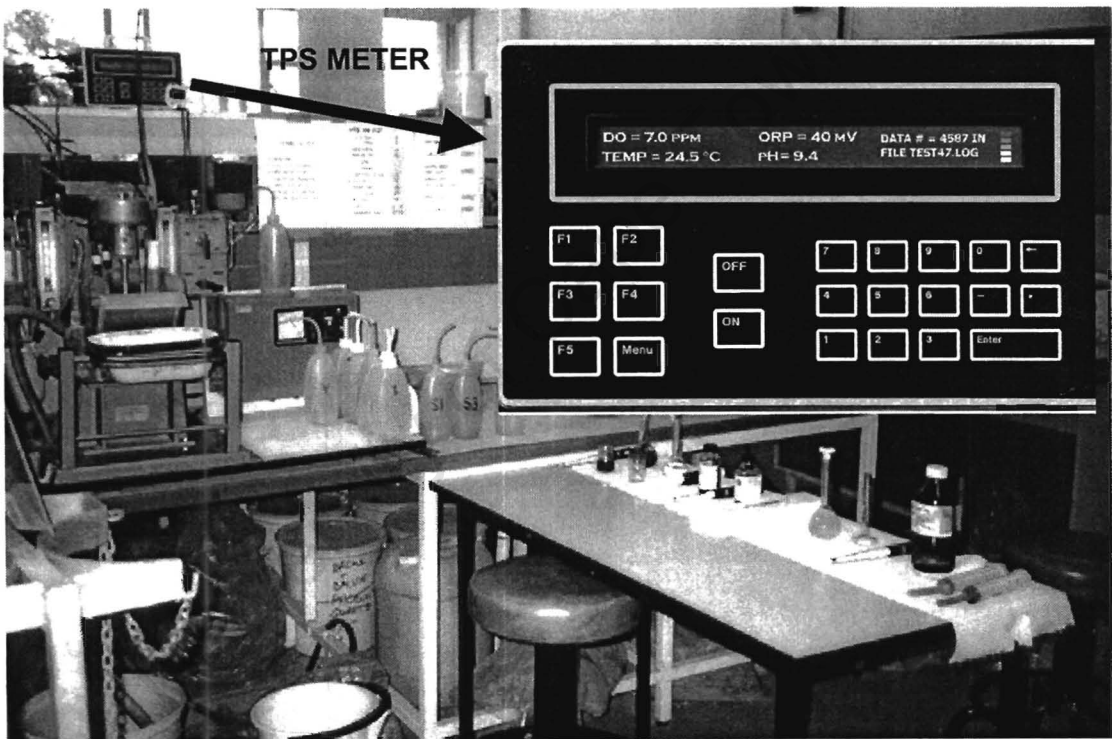


Figure 3-2: Pictorial of TPS meter used in the monitoring of pulp chemistry

3.1.3. Flotation Procedure

3.1.3.1. Milling

Milling curves were established with both stainless steel and mild steel rods (see Milling Curves in appendix A). This was used to determine that 8 minutes milling time was required to obtain a flotation feed particle size distribution of 45% passing 75 μm for stainless steel (SS) rods. For mild steel (MS), a milling time of

11 min was required for the same particle size distribution.

Immediately prior to a test, a 1 kg sample was removed from storage in the freezer and milled at 60% solids density with either MS or SS charge to obtain the required particle size distribution. The make up water added to the mill to obtain the required solids density was ordinary UCT tap water.

3.1.3.2. Batch Flotation Procedure

The standard batch flotation procedure adopted for the flotation of Merensky ore was supplied by Impala Platinum. The conditioning times in the procedure were increased so as to accommodate for the changes in gas addition required by this study. Furthermore, the duration of all tests was equal, irrespective of conditioning gas used. The TPS recording system commenced once the pulp was added into the flotation cell, and pH, DO, temperature and ORP were monitored continuously throughout the flotation test.

Stepwise Procedure:

The milled 1 kg sample was transferred to the flotation cell and tap water was added to obtain a flotation cell pulp density of 30%. The pH was not adjusted and flotation was carried out at the natural pH of approximately 10. Impeller speed in the cell was set to 1200 rpm for all tests. The pulp was conditioned under a stirred impeller for 5 minutes to allow the pulp measurements to stabilise. A dosage of 50 g/t of copper sulphate as 1% solution was then added to the pulp. The pulp was then allowed to condition for a further 5 minutes. The frother, SF7000, was added at a dosage of 80g/t together with the collector mixture of SIBX / nC4-DTP at a combined dosage of 45 g/t. The pulp was allowed to condition for a further 5 minutes. Depressant, IMP4, at a dosage of 100g/t was added as a 1% solution and conditioned for 1 minute. Thereafter, a further 5 minutes of conditioning time was specified to allow for any further gas addition (NA – *nitrogen conditioning after reagents*). The flotation gas (air or nitrogen) was then turned on at a flowrate of 6l/min and an induction period of 2 minutes was allowed before concentrate collection by scraping commenced. The froth scraping interval was 10 seconds, and 5 concentrates were collected at intervals of 1, 3, 5, 10 and 20 minutes. The wet concentrates were weighed to calculate water and mass recoveries. The concentrate, feed and tails samples were subsequently filtered, dried and weighed. Samples were analysed for copper,

nickel and iron using atomic adsorption analysis. A step by step representation of the flotation process can be seen in Figure 3-3 below.

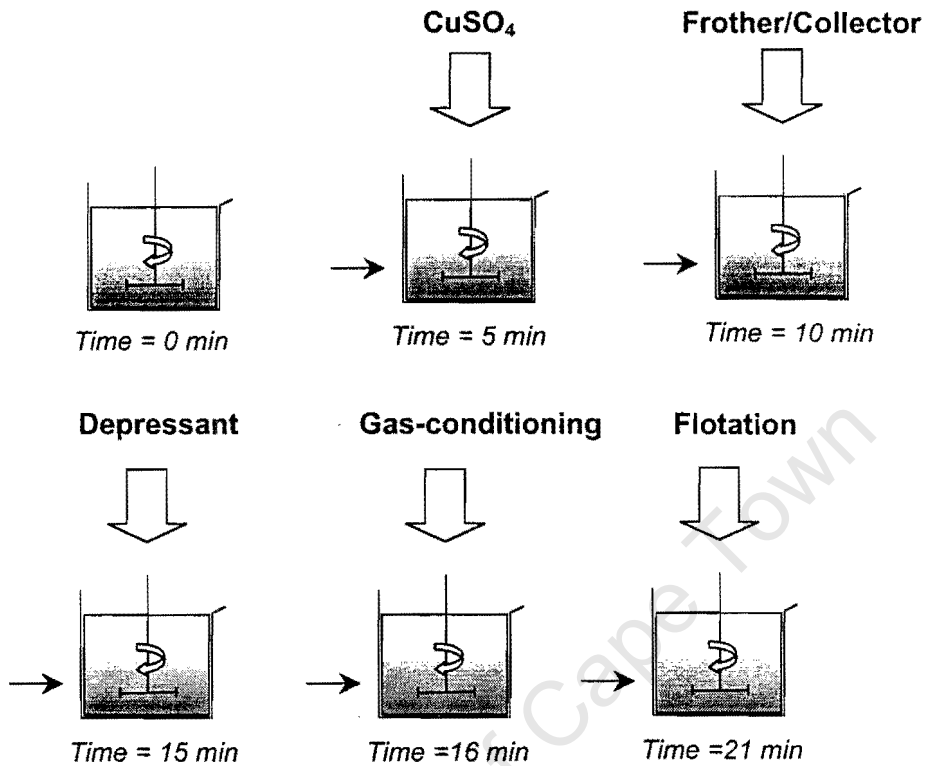


Figure 3-3: Step by step representation of the batch flotation procedure

3.2. Experimental Programme

The experimental programme was set out so that ANOVA (Analysis of variance) techniques could be used to evaluate;

- The effect of nitrogen conditioning
- The effect of nitrogen flotation
- The effect of milling media on the role of nitrogen

The experimental program is presented in Table 3-1, followed by detailed results of the batch flotation tests.

Table 3-1: Experimental programme for flotation tests (SS and MS)

Test No.	Milling Media	Code	Conditioning Gas	Flotation Gas
SF1 SF2	SS SS	STD	None	Air
SF3 SF4	SS SS	NF	None	N ₂
SF5 SF6	SS SS	NA,NF	N ₂	N ₂
SF7 SF8	SS SS	NA	N ₂	Air
MF1 MF2	MS MS	STD	None	Air
MF3 MF4	MS MS	NF	None	N ₂
MF5 MF6	MS MS	NA,NF	N ₂	N ₂
MF7 MF8	MS MS	NA	N ₂	Air

Table 3-1 shows, for example, that test SF1 and SF2 were done using pulp obtained by milling with stainless steel media, that no special gas was used during the conditioning process, and that flotation was carried out using air. Finally, it shows that these experimental conditions are referred to as STD, and that this notation will be used to identify tests carried out under these conditions in both the tables, and figures of results.

The results are presented in terms of metallurgical results (Table 3-2), the statistical analysis and significance of the effects (Table 3-3) and the pulp chemistry measurements (Table 3-4). The 'initial' results represent values after 1 min of flotation while the 'final' results represents values after the full 20 min of flotation.

Table 3-2: Summary of metallurgical results - Batch Flotation

Test No.	Milling Media	Code	Mass Pull (%)		Nickel				Copper				Iron			
					Initial		Final		Initial		Final		Initial		Final	
			Initial	Final	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery	Grade
SF1	SS	STD	0.03	2.2	0.9	6.0	58.0	5.65	5.8	13.1	75.8	2.56	0.4	24.9	15.1	15.9
SF2	SS	STD	0.05	2.4	1.4	6.0	56.6	4.55	7.6	8.0	83.6	1.71	0.3	23.1	10.9	14.7
SF3	SS	NF	0.12	2.7	2.9	4.6	65.5	4.59	12.1	8.3	70.5	2.13	0.8	18.8	11.8	11.7
SF4	SS	NF	0.24	2.8	8.7	6.4	61.4	3.89	22.8	7.5	71.8	2.04	1.4	16.0	8.6	8.4
SF5	SS	NA.NF	0.22	2.2	8.6	5.3	55.2	3.51	22.0	5.3	78.1	1.94	1.6	17.2	10.4	11.8
SF5	SS	NA.NF	0.47	3.4	14.1	4.7	51.9	2.40	34.8	4.9	79.5	1.52	2.7	16.2	12.1	9.8
SF7	SS	NA	1.14	3.5	38.3	6.6	73.1	4.11	48.5	3.3	74.9	1.70	4.9	12.0	14.5	11.7
SF8	SS	NA	0.15	3.1	5.1	6.5	73.1	4.38	14.9	7.5	85.2	2.02	1.2	21.3	16.8	13.8
MF1	MS	STD	1.0	4.6	37.8	6.7	69.3	2.82	54.2	3.5	84.8	1.27	5.0	18.9	13.9	12.1
MF2	MS	STD	1.7	5.4	57.7	6.6	78.8	2.81	70.9	3.1	87.2	1.19	9.7	18.2	21.2	12.4
MF3	MS	NF	1.5	6.7	53.1	7.1	77.7	2.28	62.7	3.1	84.0	0.91	6.1	14.6	16.5	8.8
MF4	MS	NF	1.7	5.8	53.3	3.6	74.3	2.25	59.6	2.5	78.1	0.95	6.2	13.3	13.9	8.6
MF5	MS	NA.NF	1.8	6.0	61.8	6.0	74.4	2.15	60.0	2.2	74.6	0.81	6.5	11.7	14.7	7.9
MF6	MS	NA.NF	1.6	5.5	65.2	7.6	77.4	2.57	62.0	2.8	77.4	1.00	6.5	15.0	13.4	8.9
MF7	MS	NA	1.8	5.6	62.3	5.7	75.7	2.19	70.2	2.7	88.3	1.07	8.8	15.3	18.9	10.2
MF8	MS	NA	1.5	5.7	62.8	7.5	75.0	2.39	66.3	3.0	81.2	0.99	5.8	13.0	16.3	9.8

Table 3-3: Summary of statistical analysis and STDEV - Batch Flotation

Percentage change in response due to changing parameter level (Effect)

PARAMETERS	Tests used	STAINLESS STEEL							MILD STEEL						
		Mass	Nickel		Copper		Iron		Mass	Nickel		Copper		Iron	
		Pull	Recovery	Grade	Recovery	Grade	Recovery	Grade	Pull	Recovery	Grade	Recovery	Grade	Recovery	Grade
Conditioning gas	N ₂ vs none NA, NA.NF vs STD,NF	5.03	2.99	-1.07	4.00	-0.32	1.85	-0.94	0.90	0.60	-0.22	-3.15	-0.11	-0.55	-1.27
Flotation gas	N ₂ vs air NF, NA.NF vs STD, NA	-0.07	-6.68	-1.08	-4.90	-0.09	-3.60	-3.57	6.55	1.25	-0.24	-6.85	0.21	-2.95	-2.60
Interaction		-4.63	-12.85	-0.22	3.65	-0.04	-0.80	1.68	-5.90	-0.70	0.31	-1.90	0.09	-0.60	0.94
Standard Deviations		4.81	1.94	0.61	4.62	0.36	2.12	1.61	4.77	3.73	0.16	3.51	0.08	2.93	0.40

Significance of Effect (NOTE: *** = > 99%, ** = 95x99%, * = 90x95% ~ = <90%)

		STAINLESS STEEL							MILD STEEL							
		Mass	Nickel		Copper		Iron		Mass	Nickel		Copper		Iron		
		Pull	Recovery	Grade	Recovery	Grade	Recovery	Grade	Pull	Recovery	Grade	Recovery	Grade	Recovery	Grade	
Conditioning gas	N ₂ vs none	~	*	*	~	~	~	~	~	~	~	~	~	~	~	***
Flotation gas	N ₂ vs air	~	***	*	~	~	*	**	~	~	~	*	***	~	~	***
Interaction		~	***	~	~	~	~	~	~	~	*	~	~	~	~	**

Table 3-4: Summary of profiles of ORP, DO, pH and Temperature - Batch Flotation

Test Number	Milling Media	code	pH	Temp (°C)	Pulp Potential (ORP) with Pt-Ag/AgCl electrode (mV)							Dissolved Oxygen (DO) (ppm)						
			26 min	26 min	5 min	10 min	10.5 min	15 min	21 min	26 min	46 min	5 min	10 min	10.5 min	15 min	21 min	26 min	46 min
			At Start of Flotation	At Start of Flotation	After Milling	After Cond.	After CuSO ₄	After Collector	After Depress.	At Start of Flotation	At End of Flotation	After Milling	After Cond.	After CuSO ₄	After Collector	After Depress.	At Start of Flotation	At End of Flotation
SF1	SS	STD	10.0	24.9	0	0	50	-50	-40	-20	25	6	6	6	6	6	7	7
SF2	SS	STD	10.1	24.8	10	10	80	-50	-40	-20	35	6	6	6	6	6	7	7
SF3	SS	NF	9.95	25.2	35	20	70	-30	-50	-40	-40	6.5	6	6	6	6	6	0
SF4	SS	NF	9.9	25.7	50	30	60	-50	-40	-20	-60	6.5	6	6	6	6	6	0
SF5	SS	NA.NF	9.9	25.3	40	40	70	-50	-25	-70	-50	6	6	6	6	6	6.5	0
SF5	SS	NA.NF	10	25.2	15	10	50	-100	-60	-100	-80	6.5	6.4	6.4	6	5.5	6.5	0
SF7	SS	NA	9.93	25.5	50	30	45	-60	-40	-100	30	6.5	6.4	6.2	6.2	0	0	6.5
SF8	SS	NA	9.88	25.4	-10	-20	15	-110	-60	-90	20	6.5	6.4	7.4	7.4	0	0	6.5
MF1	SS	STD	9.71	25.0	-38	-52	-40	-150	-135	-145	-25	0.5	0.5	0.5	0.5	0.5	6.5	6.5
MF2	MS	STD	9.86	25.2	-70	-70	10	-135	-135	-130	-45	0.5	0.5	0.5	0.5	0.5	6.5	6.5
MF3	MS	NF	9.92	25.1	-120	-120	0	-210	-190	-180	-250	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MF4	MS	NF	9.9	25.5	-50	-60	20	-200	-150	-155	-240	0.5	0.5	0.5	1	0.5	0.5	0.5
MF5	MS	NA.NF	9.88	24.9	-160	-140	-230	-220	-200	-245	-280	0.5	0.5	0.5	0.5	0	0	0
MF6	MS	NA.NF	9.96	24.3	20	0	-30	-130	-110	-100	-120	0.5	0.5	0.5	0.5	0.5	0	0
MF7	MS	NA	9.87	25.7	-30	-40	20	-120	-120	-150	-45	0.5	0.5	0.5	0.5	1	6.5	6.5
MF8	MS	NA	9.91	24.1	-50	-50	-5	-200	-160	-200	-90	0.5	0.5	0.5	0.5	0.5	6.5	6.5

3.3. Statistics and Reproducibility

All flotation tests were done in duplicate. The experiments were designed so that the results could be statistically analysed. For this analysis, 2^3 factorial designs were extracted from the total data set. In each set of 8 tests, 3 factors could be tested at 2 levels. The analysis of variance (ANOVA) was set up so that the first two factors (conditioning gas, and flotation gas) were the varying parameter levels (e.g. high-low), while the third factor was the reproducibility (which was possible as each test was done in duplicate). A 2^3 factorial design experiment is readily amenable to an ANOVA analysis, and this was used to evaluate the significance of the effects due to changes in parameters, as well as to calculate the standard deviation (through calculation of the residual error).

The differences in flotation behaviour with respect to changes in milling media were assessed by an evaluation of the 'T-test' between the different conditions.

A summary of the standard deviations is presented in Table 3-3 with the changes in performance (effects). The magnitude of each effect can be compared to the standard deviation to test the significance. The standard deviations should also be read in conjunction with the metallurgical results to obtain the relative standard deviation. For example, the final copper recovery for test STD_(i) is $75.8\% \pm 4.6$ and the grade is $2.6\% \pm 0.36$. Appendix D shows detailed examples of ANOVA and T-test calculations. The figures presented in section 3.4 and 3.5 below plot the average of duplicate tests, with appropriate error bars. Individual test results can be found in Table 3-2 and appendix E.

3.4. Nitrogen Added as a Conditioning or Flotation Gas After Milling with Stainless Steel Media

The effect of nitrogen addition as a conditioning gas and flotation gas is presented here for tests using ore milled with stainless steel milling media. The results are presented separately for each of the major sulphide elements, Cu, Ni and Fe. These represent the major sulphides present in the ore; chalcopyrite (Cu), pentlandite (Ni) and pyrrhotite (Fe, as an approximate representative since Fe occurs in pyrrhotite, chalcopyrite, pentlandite as well as non-sulphide gangue). The effect of nitrogen on the mass pull is presented after the individual metallurgical results.

3.4.1. The Effect of Nitrogen Addition on Nickel Bearing Minerals

Figure 3-4 shows that the highest nickel recovery was obtained with nitrogen

conditioning followed by air flotation (NA). The final recoveries obtained for tests with nitrogen flotation (NF) were higher than the standard, but with a lower final grade.

The lowest grade vs. recovery curve was achieved with nitrogen conditioning and flotation (NA.NF). The recoveries were slightly lower than those obtained at standard conditions and were accompanied by a loss in final grade. This demonstrates the nickel bearing mineral's requirement of the presence of some oxygen during either conditioning and / or flotation.

Table 3-3 shows the results of the statistical analysis, the % change, as well as the significance of the effects (evaluated after taking into account the deviation due to experimental error).

The effect of nitrogen conditioning was found to be only mildly significant (a 90% confidence level) with the effect being ~3.0%. This was the result of the negative interaction between the NA and the NA.NF tests caused by the large discrepancy in the duplicates for the NA.NF tests (viz., the poor repeatability of the NA.NF test, when used in an ANOVA analysis, lowers the statistical significance of any test it is used in combination with). The 'T' test (which is a one-on-one direct comparison that ignores interactions) comparing standard conditions to nitrogen conditioning concluded that the increase in final recovery for NA was significant at the >99.9% level. This beneficial effect of nitrogen conditioning can also be seen in Figure 3-4.

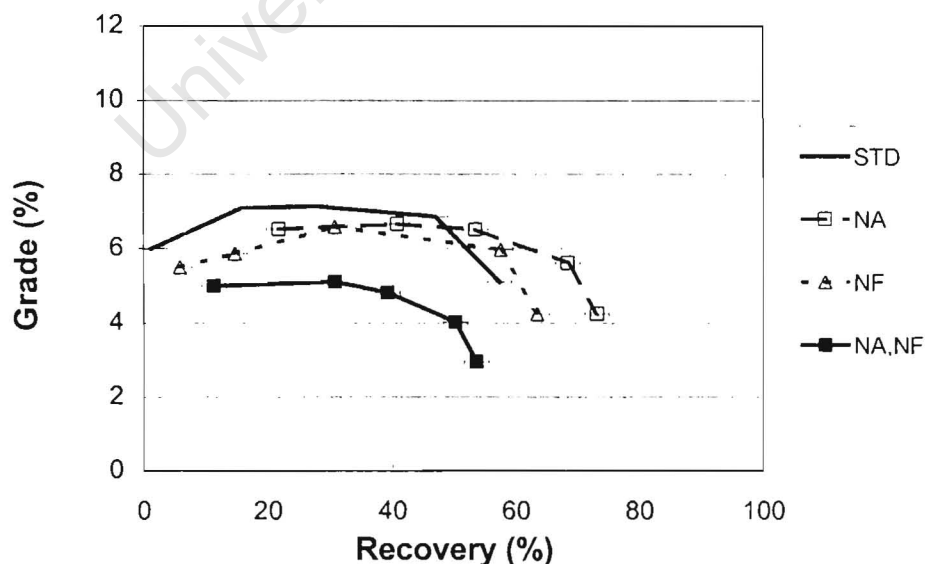


Figure 3-4: The effect of nitrogen addition to average nickel grade vs. recovery after milling with stainless steel media

The decrease in grade observed with the use of nitrogen was mildly significant for both the NA and NF cases. The interaction was not significant due to the large standard deviation associated with these tests.

The NF and NA.NF interaction, which in an ANOVA analysis correlates the overall effect of nitrogen flotation, was highly significant (>99%). Once again, the poor NA.NF result masks the analysis of NF (nitrogen flotation), and the effect of NF alone cannot be assessed by ANOVA techniques.

3.4.2. The Effect of Nitrogen Addition on Copper Bearing Minerals

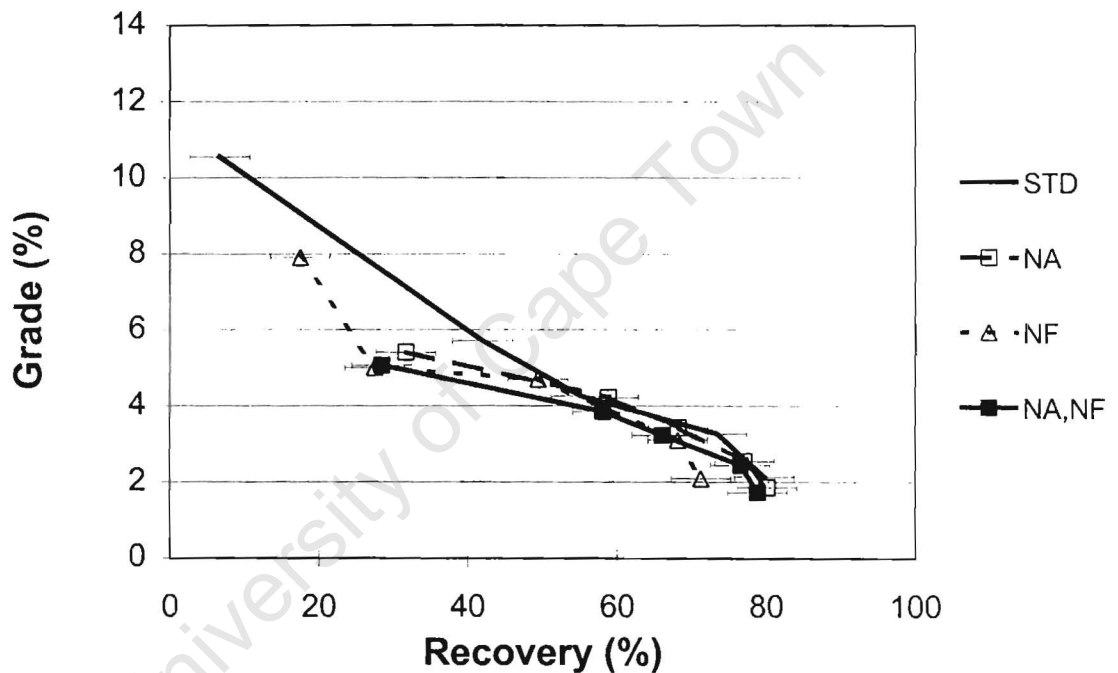


Figure 3-5: The effect of nitrogen addition to average copper grade vs. recovery after milling with stainless steel media

Chalcopyrite (CuFeS_2) is readily floatable and the effect of nitrogen is not expected to have a strong effect on copper grade and recovery. Figure 3-5 shows that the only effect is on initial grade vs. recovery. Final grades and recoveries are similar.

The high variation within the replicates themselves meant that it was not possible to draw any significant conclusions from the copper results since the grade vs. recovery curve obtained with the use of nitrogen lies on either side of the standard. This is also shown in the statistical analysis, with the effect of nitrogen conditioning or flotation showing no significance for neither NA, NF nor NA.NF.

No significant effect due to nitrogen addition was reported for the final grades as shown in Table 3-3. The copper results do not show the same trends as the nickel results, where the lowest performance was obtained with nitrogen conditioning and flotation (NA.NF), and demonstrates the apparent lack of effect of nitrogen on the flotability of copper minerals.

3.4.3. The Effect of Nitrogen Addition on Iron Bearing Minerals

Iron occurs in the gangue as well as in sulphides, and so the recovery associated with iron is low while the measured standard deviation is high (sum of errors).

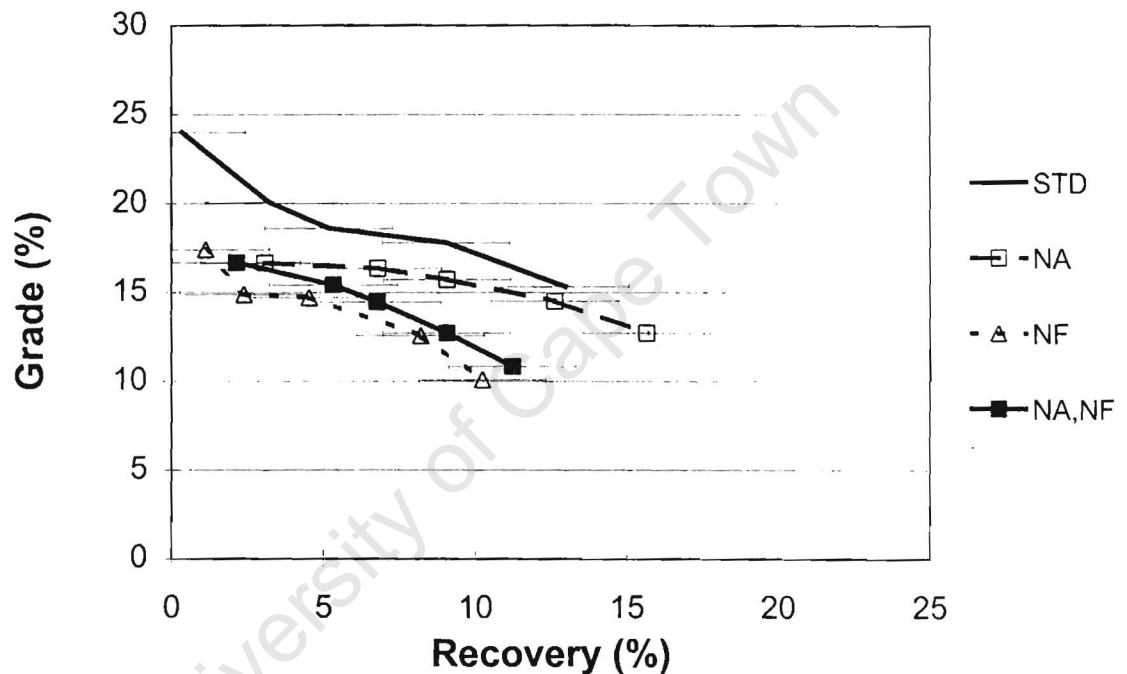


Figure 3-6: The effect of nitrogen addition to average iron grade vs. recovery after milling with stainless steel media

Figure 3-6 shows that the iron grade vs. recovery did not always follow the classical grade-recovery curve, especially during the initial stages of the test (viz., STD and NF). As was the case for copper, the variation between the replicates was large, and no obvious conclusion can be drawn from the data. The grades however were consistently lower for all floats with the presence of nitrogen. This may demonstrate the need for oxygen in the flotation of sulphide minerals that are rich in iron (viz., pyrrhotite), or may be as a result of an increase in mass pull associated with the use of nitrogen.

3.4.4. The Effect of Nitrogen Addition to Mass Pull

The mass pull results are shown in Table 3-2: Summary of metallurgical results. The high variation between the NA.NF replicates causes the statistical analysis to be inconclusive (Table 3-3: Summary of statistical analysis and standard deviations – batch flotation). However, there are indications in the data that the use of nitrogen increased the mass pull, and as expected this was accompanied by lower grades for all minerals compared to the standard flotation method. No significant effects were shown by the statistical analysis in Table 3-3, however, due to the high standard deviation.

3.5. Nitrogen Added as a Conditioning and Flotation Gas after Milling with Mild Steel Media

In general, considerably higher mass pulls were obtained in flotation tests using ore milled with mild steel milling media than in tests which used stainless steel milling media and this resulted in higher recoveries and lower grades. The rates of recoveries were also considerably higher after mild steel milling (viz., mean initial mass pull for nitrogen flotation with mild steel milling of 1.60 % vs. mean initial mass pull for nitrogen flotation with stainless steel milling of 0.18 %). The results of these tests are shown together with those of stainless steel milling media in Table 3-2: Summary of metallurgical results, Table 3-3: Summary of statistical analysis and standard deviations – batch flotation and Table 3-4: Summary of profiles of ORP, DO, pH and temperature - batch flotation.

An interesting pre-note, is that the metallurgical results for mild steel standard flotation conditions (STD, MS) compared similarly to stainless steel milling with nitrogen conditioning (NA, SS), both resulting in similar final nickel recoveries viz. 74.1 % (STD,MS) vs. 73.1 % (NA,SS) for mean nickel recoveries, although the mass pulls and rates of recoveries were different for both sets of results. The ORP's at the start of flotation were -130 mV (STD,MS) vs. -95 mV (NA,SS). These values represented the highest ORP's obtained for mild steel tests and the lowest for the stainless steel tests.

3.5.1. The Effect of Nitrogen Addition on Nickel Bearing Minerals after Mild Steel Milling

Figure 3-7 shows that the recovery vs. grade curves obtained for all the tests employing nitrogen gas lie within the same recovery range; between the results

obtained at standard conditions (STD). The final grades, however, were lower than those obtained for the standard conditions (STD).

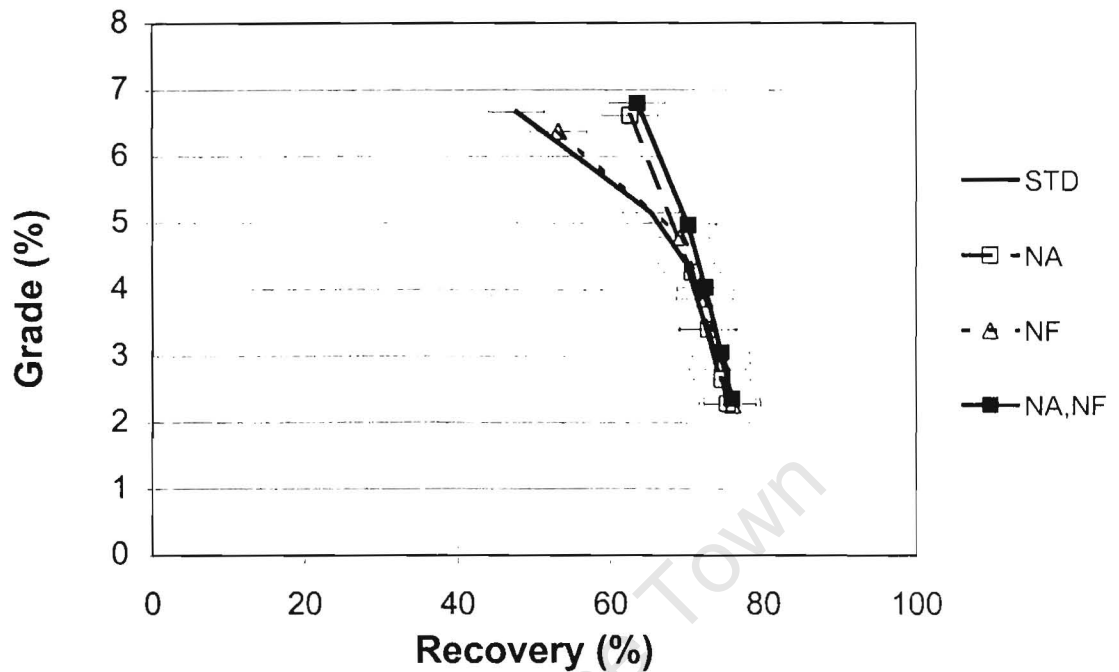


Figure 3-7: The effect of nitrogen addition to average nickel grade vs. recovery after milling with mild steel media

The decrease in grades due to the effect of nitrogen (NA and NF) was found to be insignificant although the interaction was significant at the 90% - 95% level. This is largely due to the high standard deviation. Note that the recoveries for the mild steel flotation tests lie in the same range as the nitrogen conditioned (NA) stainless steel floats, viz. 70% - 77%. The grades for the mild steel floats were however considerably lower. The case of NA.NF achieved lowest recovery and grades with stainless steel but not with mild steel. This indicates that there are other reactions occurring that are affecting the behaviour of the minerals.

3.5.2. The Effect of Nitrogen Addition on Copper Bearing Minerals after Mild Steel Milling

Figure 3-8 illustrates the high recoveries and low grades associated with mild steel milling. The scale is kept the same as Figure 3-5 (stainless steel milling media) to highlight this. The copper recovery decreased for all cases of nitrogen addition; for nitrogen conditioning (NA), nitrogen flotation (NF), and the combination of nitrogen conditioning and flotation (NA.NF). Nitrogen conditioning and flotation (NA.NF) gave the lowest set of recovery vs. grade curves, which

was not the case with NA.NF with stainless steel milling.

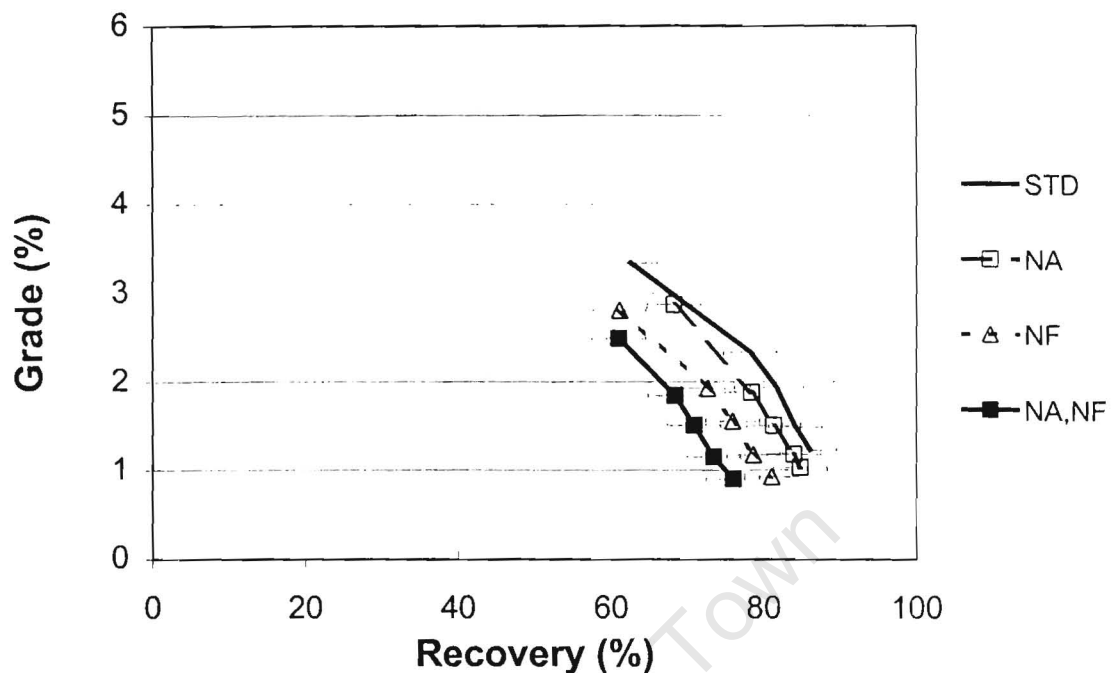


Figure 3-8: The effect of nitrogen addition to average copper grade vs. recovery after milling with mild steel media

Both these visual observations were confirmed by the statistical analysis. The negative effect of nitrogen on recovery was mildly significant (90-95% level) and the negative effect on grade was strongly significant (> 99% level).

Looking at general trends of performance, the standard floats gave the highest recovery (with both replicates taken into account) followed by the NA, NF and finally the NA.NF. This adds weight to the argument that, if anything, nitrogen depresses copper flotation (after mild steel milling). Generally, chalcopyrite will float irrespective of gas, but with mild steel milling, the sensitivity and selectivity of the copper minerals seems to have increased.

3.5.3. The Effect of Nitrogen Addition on Iron Bearing Minerals after Mild Steel Milling

Figure 3-9 shows that the recovery vs. grade curves are lower for NA.NF and NF than for standard conditions. Unfortunately, the variation in recoveries was large, and no clear conclusion can be made except to say that the use of nitrogen seems to depress the flotation of iron. The statistical analysis, due to the high standard deviations with respect to recovery, concludes that the effects are insignificant.

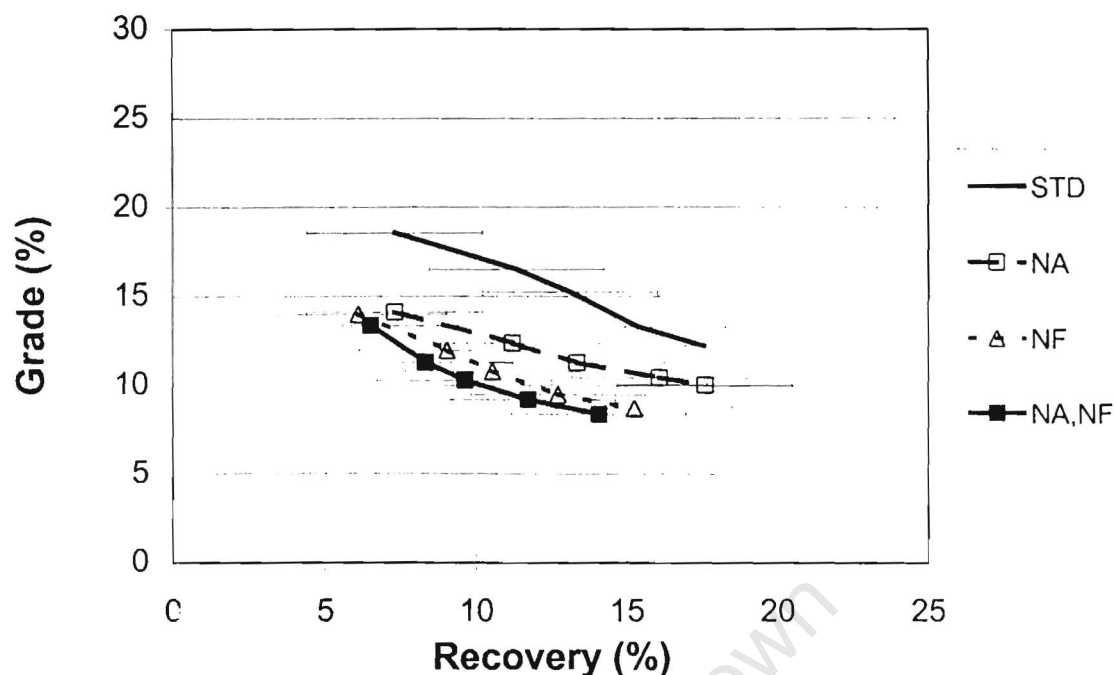


Figure 3-9: The effect of nitrogen addition to average iron grade vs. recovery after milling with mild steel media

Nitrogen addition also reduced grades and the lowest performance was obtained with NF and NA,NF. The statistical analysis showed that the negative effect on grade was highly significant (99% level). In comparison, the stainless steel results showed the lowest performance with NF.

3.5.4. The Effect of Nitrogen Addition and Mild Steel Milling to Mass Pull

The effect of milling media on flotation mass pull was strongly significant (99% level). For all cases, the effect of changing the milling media from stainless steel to mild steel resulted in a large increase in mass pull over and above the effect of the nitrogen. The mass pull obtained with mild steel was almost twice that obtained with stainless steel.

Furthermore, the large mass pull accounts for the decreased grade observed with mild steel milling media in comparison to the grades observed when stainless steel was used as the milling media.

3.6. Key Findings with Regard to Metallurgical Flotation Performance

The effect of nitrogen addition on flotation performance was evaluated at two points in the flotation process; Firstly, in the conditioning process where the mineral surface has its first interaction with the flotation chemicals, and secondly, as the gas for flotation. Combinations of both were also employed.

Based on results, the following observations regarding the effect of nitrogen were made;

Effects on individual metal recoveries

1. Nitrogen conditioning with stainless steel milling results in a recovery benefit for nickel bearing minerals.
2. Nitrogen addition (as either conditioning or flotation gas) had no significant effect on copper flotation when using stainless steel milling media.
3. The combination of nitrogen conditioning and nitrogen flotation resulted in the depression of iron, when using stainless steel milling media.

General observations

4. When both nitrogen conditioning and flotation were employed in the flotation of stainless steel milled ore, a general depression of all sulphides was observed.
5. The use of mild steel milling resulted in a reducing environment characterised by high mass pulls but correspondingly low grades.
6. With mild steel milling media, the use of nitrogen led to decreased grades for all base metal sulphides. For stainless steel media, statistical analysis showed that the use of nitrogen in certain instances resulted in increased mass pulls (corresponding to lower grades).

The aspects of flotation chemistry that are possibly affected by nitrogen addition, and how they manifest themselves as points 1 to 6 above is discussed in the literature review (see section 2.4.2 to 2.4.6) and the following key questions arise from the literature and the metallurgical results.

- Nitrogen addition and milling with mild steel media both reduce DO and ORP levels, yet result in differing effects on flotation performance. Why is this... ?

- Is the removal of oxygen the reason for the observed behaviour? Furthermore, what are the underlying mechanisms affected by the removal of oxygen that result in the observed behaviour?
 - ⇒ Is there a reduction in mineral surface - collector interaction, caused by hindered collector oxidation... ?
 - ⇒ Does reduced mineral oxidation as a result of nitrogen conditioning lead to improved nickel flotation... ?
 - ⇒ Are galvanic interactions reduced... ?
 - ⇒ Does nitrogen affect the mineral surface - collector - activator (copper sulphate) interaction and / or the type of collector products formed... ?
 - ⇒ Does nitrogen have a direct or indirect effect on the nature of the froth chemistry and mobility via its interaction with the pulp chemistry... ?
- Finally, why does nitrogen not benefit flotation performance when used in conjunction with mild steel milling media... ?

In order to increase our understanding of the behaviour of nitrogen in batch flotation and answer the above questions, the following complementary investigations were initiated; investigating the role of nitrogen on measurable properties of the pulp chemistry, investigation of mineral surface oxidation in the presence of nitrogen, and finally, attempting to follow the collector – mineral interaction under flotation test conditions.

4. ELUCIDATION OF MECHANISMS VIA COMPLEMENTARY STUDIES

In order to elucidate the behaviour of nitrogen in flotation pulps, three sets of complimentary investigations were carried out. Firstly, a closer investigation of the results of the pulp chemistry measurements was carried out. Secondly, measurements of residual xanthate by UV spectroscopy were conducted. Finally, the metal hydroxide on the mineral surface was measured by a technique employing EDTA (ethylene diamine tetra acetic acid) for the purposes of extraction.

The results of each of these investigations follow.

4.1. The Effect of Nitrogen on Pulp Chemistry Measurements

Pulp chemistry profiles of pH, temperature, dissolved oxygen (DO) and oxidation reduction potential (ORP, measured with a Pt - Ag/AgCl electrode) were recorded for each flotation test so as to monitor the changes in the pulp chemical environment. Data logging started at the initial mixing time, through conditioning and continuing up to the end of flotation. Sample data points were recorded every 10 seconds during a typical 45 minute flotation session. Table 3-4 shows a summary of the results. The full graphical information for each test is shown in Appendix B.

The ORP profiles showed measured responses to milling media, activator addition, collector addition and gas addition. The DO profiles showed the response to milling media and gas addition. Flotation pulps milled with mild steel milling media had significantly lower ORP and DO levels than those milled with stainless steel media.

The ORP profiles showed a characteristic increase on addition of activator (CuSO_4 at $t=10\text{mins}$) demonstrating the oxidising nature of CuSO_4 and a sharp decrease to more reducing conditions on collector addition ($t=15\text{mins}$) due to the presence of the xanthate anion.

When nitrogen was used in either conditioning or flotation, the DO profile showed a drop in dissolved oxygen levels to near zero as a result of purging of oxygen from the system.

Tests milled using mild steel media resulted in lower ORP's and DO's after milling. For these tests, DO levels increased once the pulp was exposed to air during the conditioning time, and reduced if nitrogen was added.

The pH and temperature were similar for both types of milling and remained fairly constant throughout the flotation process, with only a small change in temperature, attributed to energy input, being recorded.

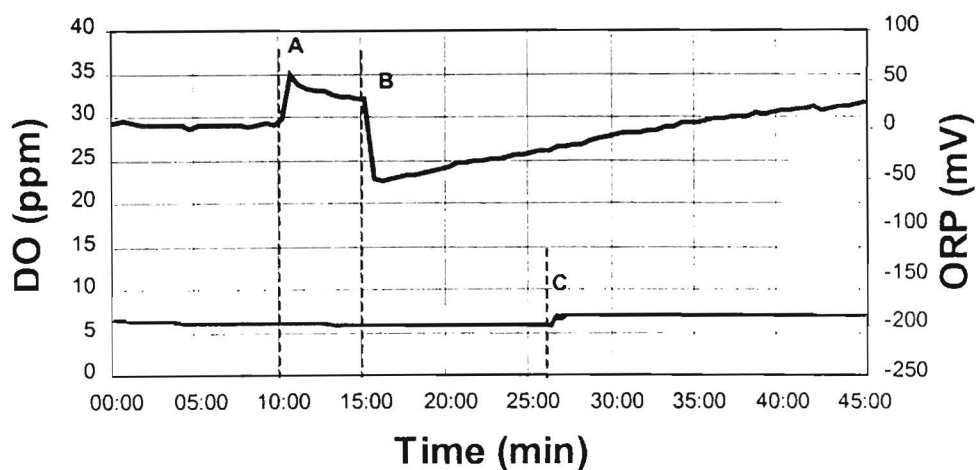
A more detailed assessment of the effect of nitrogen on the measured pulp chemistry is presented below.

4.1.1. Flotation Tests with Stainless Steel Milling Prior to Flotation

The pH, temperature, DO and ORP were monitored for the duration of the flotation tests, albeit that the temperature and pH were largely unchanged.

Figure 4-1 shows the measured profiles for the standard flotation test, and for the test where nitrogen was used during flotation.

Standard Flotation after milling with Stainless Steel Media



A = CuSO₄ addition, B = Collector addition, C = Start of Flotation

--- DO (ppm)
 — ORP (mV)

Nitrogen Flotation after milling with Stainless Steel media

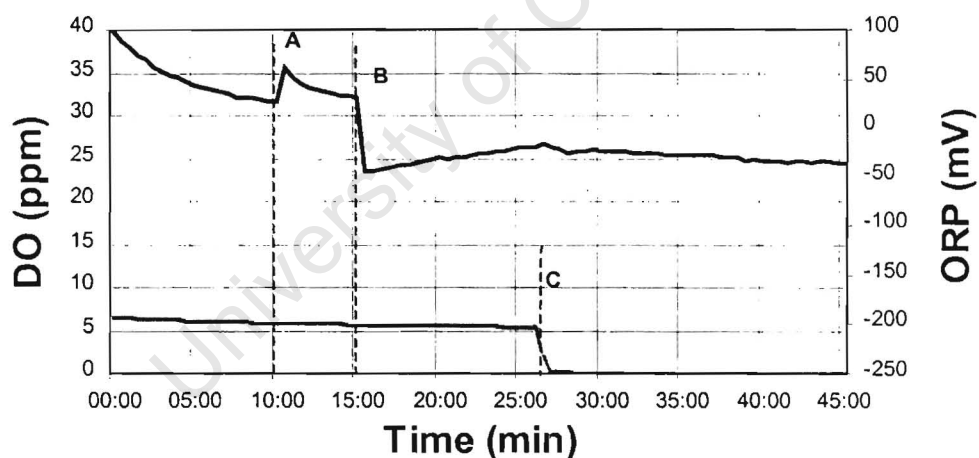


Figure 4-1: Sample pulp chemistry profiles for tests milled with stainless steel milling media; standard flotation test (top) & test using nitrogen as flotation gas (bottom)

Table 4-1 shows the ORP's and DO's at key times through the tests. The abbreviations for the test conditions shown below are as explained in Table 3-1: Experimental programme for flotation tests (SS and MS).

Table 4-1: Summary of pulp chemistry measurements, stainless steel media.

	ORP* measured with a Pt – Ag/ AgCl electrode (mV)			
	After Milling	After reagents	At start of flotation	At end of flotation
STD	25	-40	-20	30
NA	25	-45	-95	25
NF	25	-45	-30	-50
NA,NF	25	-50	-85	-65
	DO* measured with a YSI probe (ppm)			
	After Milling	After reagents	At start of flotation	At end of flotation
STD	6	6	7	7
NA	6	0	0	7
NF	6	6	6	0
NA,NF	6	0	0	0

* Average value of duplicate tests

The pH was consistent at a value of approximately 10 pH units, while the temperature increased with time, and generally ranged between 20 °C from after milling to 25 °C at the end of flotation (the rise due to energy input via mixing). The DO was generally 6 ppm - 6.5 ppm, with nitrogen conditioning or flotation reducing it to 0 ppm.

The pulp potentials (ORP's) were between 0 mV - 50 mV after milling and were found to increase with copper sulphate addition. Subsequently, the addition of collectors (SIBX and nC4-DTP) caused a reduction in ORP's. Further reductions were observed with nitrogen conditioning or flotation. Final ORP's were dependant on flotation gas, with air flotation resulting in values ranging between 20 mV to 35 mV while the use of nitrogen as flotation gas resulted in values ranging between -20 mV to -80 mV, depending on the type of initial conditioning gas.

4.1.2. Flotation Tests with Mild Steel Milling Prior to Flotation

Figure 4-2 shows the measured pulp chemistry profiles for the standard flotation test, and for the test employing nitrogen during flotation. The milling media used in this case was mild steel.

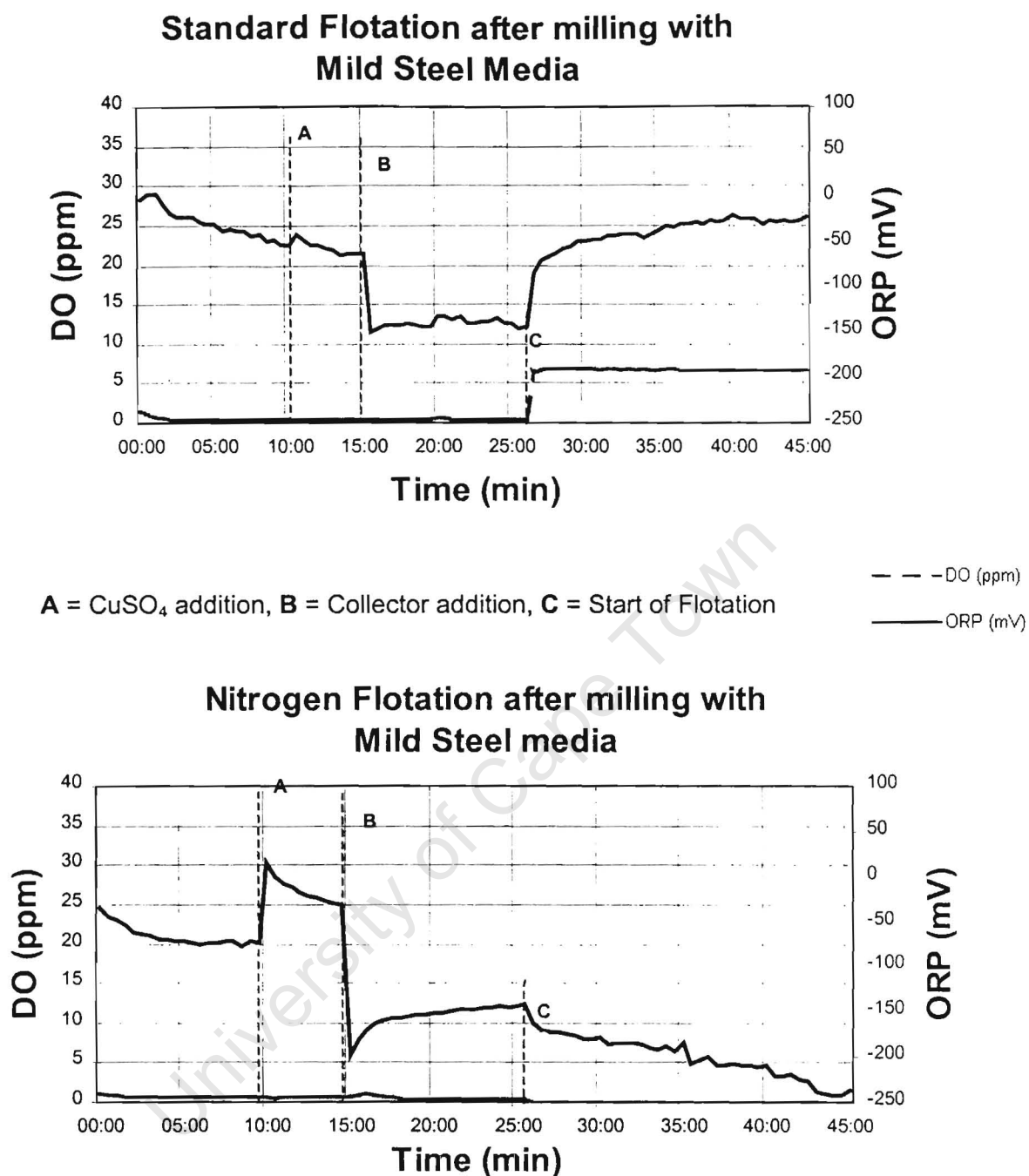


Figure 4-2: Sample pulp chemistry profiles for tests milled with mild steel milling media; standard flotation test (top) & test using nitrogen as flotation gas (bottom)

Table 4-2 shows the ORP's and DO's at key times through the tests employing mild steel milling media. As with the stainless steel tests, the pH was consistent at approximately 10, while the temperature increased with time and generally ranged between 20 °C - 25 °C from after milling to end of flotation. The milling media, however, had a pronounced effect on the DO and ORP values.

Table 4-2: Summary of pulp chemistry measurements, mild steel media.

	ORP* measured with a Pt – Ag/ AgCl electrode (mV)			
	After Milling	After reagents	At start of flotation	At end of flotation
STD	-70	-135	-130	-45
NA	-90	-170	-175	-68
NF	-70	-155	-168	-245
NA,NF	-45	-140	-173	-200
	DO* measured with a YSI probe (ppm)			
	After Milling	After reagents	At start of flotation	At end of flotation
STD	0.5	0.5	6.5	6.5
NA	0.5	0.5	6.5	6.5
NF	0.5	0.5	0.5	0.5
NA,NF	0.5	0.5	0	0

* Average value of duplicate tests

The DO was always low (0.5 ppm) and only with air flotation was it increased to 6.5 ppm. Nitrogen during conditioning or flotation reduced it to 0 ppm.

The average ORP was -70 mV after milling in mild steel which was substantially lower than obtained after stainless steel milling. Addition of copper sulphate caused an increase in ORP, which was subsequently reduced with collector (SIBX:nC4-DTP) addition, and still further if subsequent nitrogen conditioning or flotation took place.

4.1.3. Key Findings From the Pulp Chemistry Measurements During Flotation Tests

The following can be stated with regard to the observed pulp chemistry profiles;

- i. The use of nitrogen resulted in the creation of less oxidising conditions, independent of the point of application (i.e. during conditioning, vs. during flotation). This was characterised by the measurement of lower DO and ORP values.

- ii. Tests using mild steel media during milling resulted in lower ORP's and DO's after milling than corresponding tests using stainless steel media. This indicates the presence of more reducing conditions with mild steel relative to stainless steel milling media. The use of nitrogen in these instances, was consistent, and resulted in further reductions in the ORP and DO levels.
- iii. It was visually observed that the extent of the ORP rise on copper addition was larger in the case of stainless steel milling relative to mild steel milling³. This may be an indication that the introduction of Cu^{++} ions in the case of mild steel milling did not affect the ion balance in the cell significantly, and could indicate the presence of another cation swamping out the effect of the copper ion.
- iv. Under standard flotation conditions, and for nitrogen conditioning, the observed ORP at the end of flotation with air was positive (between 20 and 35 mV $E_{\text{Ag/Cl}}$) and above the minimum required for dithiolate formation (between -2 and -22 mV, see c.f. 2.6.2). With the use of nitrogen during flotation, however, the potential was below the limits for dithiolate formation indicating the possible hindrance of collector mineral interactions.
- v. No conclusion pertaining to the effect of nitrogen on mineral surface oxidation could be extracted directly from the pulp chemistry profiles, due to the fact that a platinum electrode was used (which measures overall solution potential), as opposed to mineral electrodes. Further investigation will be required to ascertain nitrogen's role in this regard.

With regard to the question of whether the effect of nitrogen is related to the creation of a reducing environment in general, or merely the removal of oxygen, the following is noted;

The use of mild steel milling resulted in a reducing environment characterised by high mass pulls but correspondingly low grades. Furthermore, the recovery obtained from the mild steel standard flotation test was in the same range as a stainless steel milled and nitrogen conditioned float (NA) viz., between 73% - 74%. The ORP and DO profiles for these tests, however, are dissimilar. This

³ This was not always visually represented in the captured data due to the time frame of the rate of data capture (every 30 seconds) and the rapid rate of decline of the CuSO_4 peak with the cell being continuously mixed.

indicates that the observed effect cannot trivially be attributed to either the creation of a reducing environment, or merely the removal of oxygen, but is rather due to a combination of these and other factors, such as the role of abraded iron in promoting high froth stability, and thus high recoveries during mild steel milling (which we shall attempt to demonstrate later in this study).

4.2. The study of the Collector – Mineral Interaction by Measurement of Residual Xanthate Levels in the Flotation Pulp

This section focuses on the study of the collector - mineral interaction. The influence of activator (CuSO_4) and ferrous iron on this interaction is assessed both in the presence and absence of nitrogen. The method adopted in this study is a well known one, and involves the measurement of residual xanthate at the concentrations experienced in flotation pulps by UV spectroscopy at 301 nm (Jones, 1991).

The objectives of this phase of work are as follows:

- i. To establish the relationship between the Merensky ore, the xanthate collector and the copper sulphate activator under normal test conditions. This involves establishing the stoichiometry of the reaction between reacting components, viz. the copper sulphate and the xanthate, and to assess how this is affected in the presence of ore.
- ii. To investigate the effect of nitrogen addition on the above relationships to ascertain whether the observed change in flotation response when nitrogen was added was due to a shift in the collector-activator-mineral interaction scheme.

Furthermore, to establish the effect of other species in the pulp on the collector – mineral – activator interaction, namely the iron species present in the pulp after mild steel milling.

This section starts off with a description of the experimental procedure and the programme formulated from the statement of objectives above. Results are then presented, followed by a discussion and interpretation of the observed phenomena. The section then ends with a summary of key results.

4.2.1. Experimental Procedure – Residual Xanthate Measurements

Samples were prepared by milling a 1 kg merensky ore sample in a laboratory mill with the appropriate charge (either mild steel or stainless steel rods). Milling conditions were the same as for the flotation tests. The sample was removed from the mill and dried by air forced filtration. The cake (5 - 10 % moisture) was then split by hand into 16 samples (75 – 100 g wet mass). These were then transferred into plastic bags and sealed (airtight) and subsequently stored in a freezer till needed. The handling time of the sample from the start of milling to storage of the samples was approximately 2 hrs.

A 300 ml beaker was set up on a magnetic stirrer and between 80g - 100g (wet mass containing approx. 10% moisture) of ore was added to it. A measured amount of de-ionised water between 240ml and 300ml (set to pH 9 to represent equivalent flotation conditions), was added so as to recreate the same pulp density in the beaker as was present during flotation (i.e. 30%). The mixer was then turned on and the slurry was left to mix for 5 minutes. If nitrogen addition was specified by the experimental conditions, then the gas was also turned on at this point (time = 0). Reagents were then added at the same concentration and conditioning times as for flotation tests, i.e. after 5 minutes the activator or ferrous ion source was added (CuSO_4 or FeSO_4 as specified), and after a further 2 minutes, the collector was added (if specified). At time=10 minutes, a sample (approximately 50 ml) was withdrawn from the solution via a syringe and immediately transferred into a vial and sealed.

The contents of the sample vial was filtered. The liquor was collected in a sample container. A quartz cuvette was filled with the liquor, and read against the blank pH 9 de-ionised water solution for the UV – visible xanthate peak at 301nm. The resulting absorbance curve was plotted, and the height of the peak was noted. This was then corrected for baseline movements caused by impurities, and a final result for the absorbance and hence concentration was calculated. A sample of the UV absorbance profile can be found in appendix G.

Preliminary tests without ore were also done to establish the baseline of the xanthate reaction with the other flotation reagents in the system, viz. copper added as activator, and the presence of ferrous iron in the pulp after milling with mild steel media.

4.2.2. Experimental Programme

Table 4-3 shows the experimental programme devised for the measurement of residual xanthate by UV, together with the observed results.

Table 4-3: Experimental programme and results for residual xanthate measurements by UV

Repeatability Experiments (Stainless Steel milled ore)

		UV absorbance	Xanthate Conc $\times 10^6$ (mol/dm ³)
UV0a	1% SIBX solution	0.73	41.94
UV0b	1% SIBX solution	0.68	38.60
UV0c	1% SIBX solution	0.71	40.44
STDEV		0.03	1.7
% Error		3.8%	

Experiments in absence of ore

Test No	REAGENTS PRESENT			Ratio [SIBX:Cu]	UV absorbance	Xanthate Conc $\times 10^6$ (mol/dm ³)
	gmols SIBX	gmols Cu ⁺⁺	Nitrogen			
UV1	1.60E-05	0.4E-05		4:1 [#]	0.27	15.54
UV2	1.60E-05	0.8E-05		2:1 [*]	0.00	0.00
UV3	1.60E-05	1.6E-05		1:1 [@]	0.00	0.00
UV7	1.60E-05	0.4E-05	✓	4:1	0.22	12.86
UV8	1.60E-05	0.8E-05	✓	2:1	0.00	0.06
	gmols SIBX	gmols Fe ⁺⁺		Ratio [SIBX:Fe]		
UV4	1.60E-05	0.4E-05		4:1	0.70	39.87
UV5	1.60E-05	0.8E-05		2:1	0.69	39.33
UV6	1.60E-05	1.6E-05		1:1	0.63	36.21

- Only half of the xanthate should react, according to the reaction $\text{Cu} + 2\text{X} \rightarrow \text{CuX}_2$

* - Stoichiometric rxn. Residual should ideally be zero according to the reaction $\text{Cu} + 2\text{X} \rightarrow \text{CuX}_2$

@ - Excess copper. Residual must be zero according to the reaction $\text{Cu} + 2\text{X} \rightarrow \text{CuX}_2$

Experiments in presence of ore (SS and MS milling media)

Test No	REAGENTS PRESENT				Ratio [SIBX:Cu]	UV absorbance	Xanthate Conc $\times 10^6$ (mol/dm ³)
	Mass ore (g) SS	gmols SIBX	gmols Cu ⁺⁺	Nitrogen			
UV S1	94	1.48E-05	0.74E-05		2:1 [*]	0.08	4.29
UV S2	89	1.40E-05	0.35E-05		4:1 [#]	0.34	19.23
UV S3	100	1.57E-05	1.57E-05		1:1 [@]	0.00	0.00
UV S4	101	1.59E-05	0.79E-05	✓	2:1	0.16	9.29
UV S5	101	1.59E-05	0.40E-05	✓	4:1	0.46	26.00
UV S6	100	1.57E-05	1.57E-05	✓	1:1	0.00	0.00
UV S0	94	1.48E-05	-			0.68	38.60

Test No	REAGENTS PRESENT				Ratio [SIBX:Cu]	UV absorbance	Xanthate Conc $\times 10^6$ (mol/dm ³)
	Mass ore (g) MS	gmols SIBX	gmols Cu ⁺⁺	Nitrogen			
UV M1	94	1.48E-05	0.74E-05		2:1	0.22	12.57
UV M2	93	1.46E-05	0.36E-05		4:1	0.44	25.14
UV M3	89	1.40E-05	0.70E-05	✓	2:1	0.28 [^]	16.00
UV M4	89	1.40E-05	0.35E-05	✓	4:1	0.56	32.00
UV M0	93	1.46E-05	-			0.58	33.14

[^] noisy spectrum

Experiments in presence of AGED ore

Test No	REAGENTS PRESENT				Ratio [SIBX:Cu]	UV absorbance	Xanthate Conc $\times 10^6$ (mol/dm ³)
	Aged SS ore (g)	gmols SIBX	gmols Cu ⁺⁺	Nitrogen			
AGED 1	94	1.48E-05	0.74E-05		2:1	0.08	4.80
AGED 1N	94	1.48E-05	0.74E-05	✓	2:1	0.14	8.01

4.2.3. Results – Measurement of Residual Xanthate by UV

The results of experiments presented in Table 4-3 above are discussed in detail below. They are presented separately for tests without ore (solution experiments) and those with ore. This is done to enhance readability and to facilitate the build up of our understanding of the process (i.e., basic stoichiometry vs. actual flotation scenario).

4.2.4. Statistics and Reproducibility

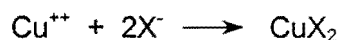
All experiments in this section of the study were conducted individually, except for a set of repeatability tests carried out at the outset. The results for these repeatability tests can be found in Table 4-3 above (As can be seen, the variation is small and the absolute error is < 4%.)

4.2.5. Study of Activator (CuSO₄) – Collector – Mineral reaction

4.2.5.1. In Absence of Ore

Results for these experiments can be found in Table 4-3, tests UV1 – UV8.

For tests UV1, UV2 and UV3, the change in copper concentration produces expected results. When a stoichiometric amount of copper is used (test UV2), the concentration of xanthate remaining in solution is nil. It follows then, that when more than the stoichiometric amount of copper is added, the xanthate concentration measured should remain as zero (test UV3), all the xanthate having precipitated out and lost in the filtration according to the reaction;



This shows that the stoichiometric ratio between copper and xanthate in the relationship is at least 1:2 .

According to the results of test UV7 and UV8, nitrogen conditioning decreases the measured free xanthate after reaction. This can be seen when comparing the half-stoichiometric tests, viz. ½ mole Cu per 2 moles X (test UV1, no nitrogen and test UV7 with nitrogen).

4.2.5.2. In Presence of Ore

The results of tests using ore obtained from stainless steel and mild steel milling

are presented Table 4-3 above.

Firstly, the Cu-X interaction shows similar results to those without ore added in the context that increasing copper dosages causes reduced concentrations of residual xanthate. However, it can be seen that the addition of ore changes the observed stoichiometric ratio between copper and xanthate. For the case of stoichiometric copper added, viz. 1 mole copper per 2 moles xanthate (test UVS1), it can be seen that xanthate is still present after reaction. A calculation of the reaction ratio between xanthate and copper in this instance yields a 1:1.8 ratio in the presence of ore, as opposed to the 1:2 ratio normally expected and observed in 2 phase.

It is possible that some copper may oxidise in the presence of ore and thus not be available for reaction with the xanthate, resulting in an observed lowered ratio.

The effect of nitrogen addition on the copper - xanthate reaction was to increase the amount of residual xanthate present significantly, implying a further decrease in the calculated stoichiometric ratio between copper and xanthate (see Table 4-3: tests UVS4 and UVS5, nitrogen vs. UVS1 and UVS2, no nitrogen). (Note: this effect of nitrogen on the stoichiometric ratio is over and above that caused purely by the addition of ore, reported above).

4.2.5.3. Effect of Ageing the Ore

Tests (AGED1 and AGED 1N) with the aged ore (24 hrs) showed that there was no significant change in residual xanthate concentration between tests using aged ore and fresh ore. The 1:1.8 ratio between collector and activator was once again observed for these tests. The nitrogen conditioning consistently resulted in higher levels of residual xanthate relative to non - nitrogenated conditioning (i.e., a substantial decrease in the stoichiometric ratio between copper and xanthate).

4.2.6. Study of Ferrous Iron on the Collector – Mineral Reaction

4.2.6.1. In Absence of Ore

The addition of varying amounts of ferrous (added as FeSO_4) and xanthate in tests UV4, UV5 AND UV6 show that very little reaction, if any, occurs for the half - stoichiometric and stoichiometric test conditions (stoichiometry for the Fe reaction is based on a hypothesised FeX_2 complex). This demonstrates that Fe and Xanthate do not interact in the same manner as copper and xanthate do in the

flotation pulp (i.e. a 1:2 ratio according to the reaction $\text{Fe}^{++} + 2\text{X}^- \rightarrow \text{FeX}_2$). A slight decrease in free xanthate is observed only in the case where twice the stoichiometric amount of Fe is used (test UV6).

Since the interaction between xanthate and Fe was found to be limited, no study employing ore was conducted.

4.2.7. Summary of Results - Residual Xanthate Measurements

The following can be concluded about the activator-collector-mineral interaction as a result of the study of residual xanthate measurements.

1. Copper and xanthate react in a stoichiometric ratio of 1:2 respectively when no other components are present in the system. The addition of ore causes the calculated stoichiometric ratio to decrease to 1:1.8, demonstrating that less copper is available for reaction with the xanthate or that the complex formed on the mineral surface is different .
2. A consistent feature of nitrogen conditioning in the presence of ore is a substantial decrease in measured residual xanthate, observed as a further decrease in the observed stoichiometric ratio between copper and xanthate. This implies either a different reaction mechanism or a stopped reaction in the presence of nitrogen.
3. No significant change in residual xanthate between tests using aged ore and those employing fresh ore was found. Nitrogen conditioning on aged ore once again resulted in increased levels of residual xanthate.
4. Little or no interaction was found to exist between Fe^{++} and xanthate at the conditions under current investigation.

4.3. The Investigation into Mineral Surface Oxidation Using Metal Hydroxide Complexation by EDTA

EDTA (ethylene diamine tetra acetic acid) is known to be a metal ion complexant and has been shown to remove surface metal hydroxides of pure minerals (Clark et.al., 1995). Subsequently, measurement of the quantities of these removed surface products can be carried out by atomic adsorption spectroscopy, resulting in a technique that has the ability to monitor the level of surface hydroxides on a mineral in some pulps. Another application of EDTA addition is in "cleaning" the

mineral surface of unwanted hydrophilic metal hydroxides so as to improve flotation behaviour. In this study, EDTA is used in order to gain an understanding of the level and nature of hydroxides on the mineral surface. It has been used successfully on pure minerals (Clark, 1995, 1997 and Grano, 1997), however, no attempt has been made to apply the technique to a complex sulphide PGM ore thus far. A limit on this process for a PGM ore is the presence of non-sulphide gangue that may swamp the target mineral and decrease the effectiveness of the process as a consequence of the high "noise to measurement" ratio. This section nevertheless describes an attempt by this study to use the technique, with appropriate modifications, to gain *qualitative* information about the nature and amounts of surface hydroxides present.

More specifically, the objectives of this phase are:

- To establish whether EDTA can be used to measure the level of surface hydroxides for a complex sulphide PGM ore containing high gangue levels.
- To establish whether the proposed reason for froth stability associated with mild steel milling is due to the high levels of iron in the pulp (c.f. 5.1 below).
- To investigate whether the addition of nitrogen during flotation tests results in reduced mineral surface oxidation either as a result of the direct effect of nitrogen or an indirect effect via galvanic interaction protection mechanisms.

4.3.1. Experimental Procedure – Measurement of Concentration of Metal Hydroxide by EDTA Complexation

Samples were prepared by milling a 1 kg Merensky ore sample in a laboratory mill with the appropriate charge (either mild steel or stainless steel rods). Milling conditions were the same as for the flotation tests. The sample was removed from the mill and dried by air forced filtration. The cake (5 - 10 % moisture) was then split by hand into 16 samples (75 – 100 g wet mass). These were then transferred into plastic bags and sealed (airtight) and subsequently stored in a freezer till needed. The handling time of the sample from the start of milling to storage of the samples was approximately 2 hrs.

The required reagents were prepared using AR grade reagents and de-ionised water set to pH 9 with NaOH. A 250 ml beaker was set up on a magnetic stirrer and between 80g - 100g ore was added to it. A measured amount of de-ionised water was added so as to recreate a 30% pulp density in the beaker as was present during flotation. The mixer was then turned on and the slurry was left to

mix for 5 minutes. If nitrogen addition was specified by the experimental conditions, then the gas was also turned on at this point (time = 0). After 5 minutes the activator was added (if specified), and after a further 2 minutes, the collector was added (if specified). At time=10 minutes, two samples (approximately 50 ml) were withdrawn from the solution via a syringe and immediately transferred and sealed into vials, labelled 'A' and 'B'.

The required amount of EDTA was added to the second sample vial, marked 'B'. The vial was then shaken vigorously for 5 minutes, and left to stand for a further 5 minutes for extraction. After this time, the sample 'B' was then filtered and the liquor was collected in a sample container. The treated solids were dried and weighed.

No EDTA was added to sample 'A'. This sample was filtered 'as is', and the liquor collected in a sample container.

Filtration was by gravity in a conical funnels with Whatman100 filters in both instances.

For subsequent AA analysis, clear liquid was then decanted from both sample containers and sent for AA analysis of metal ions (iron, copper and nickel). Together, the results of the two were used to calculate the concentration of metals complexed with EDTA, for the sample mass treated. (i.e. the difference between tests with EDTA (sample B) and that without EDTA (sample A)).

4.3.2. Preliminary Experiments

Due to the lack of a previously validated experimental technique, preliminary experiments were conducted so as evaluate the possibility of the use of a technique for PGM bearing ores. The main concern with the application of this technique to a complex sulphide pgm ore is the high ratio of gangue to sulphide mineral. Furthermore, no prior knowledge of the concentrations of EDTA needed for extraction was available. The main issues thus needing to be resolved were whether EDTA could be used to complex metal hydroxides present on the particle surface, and if so, what dosage of EDTA would be required to achieve this.

Table 4-4 shows the results of preliminary experiments obtained with stainless steel milled ore. The results, reported as metal extracted per gram mineral treated, show that little or no metal has been complexed. This is explained by the large amounts of gangue mineral depleting EDTA, leaving none available for complexation with the target minerals.

Table 4-4: Preliminary measurements of metal abstracted by EDTA - level 1

Test No:	EDTA dosage (μ l)	Metal abstracted (mg Fe/g mineral)	Metal abstracted (mg Cu/g mineral)	Metal abstracted (mg Ni/g mineral)
E15a	108	0.0030	0.00007	0.00022
E15b	108	ND	0.00003	0.00004

ND – Not detectable

In order to evaluate the EDTA dosage necessary to accommodate for the high amount of gangue, dosages of 1080 μ l and 10800 μ l (10 times and 100 times the dosage used in the level 1 experimental programme) were used in the next set of experiments (level 2). If the dosage of EDTA was adequate, then one would expect a graph of increasing "metal extracted" initially, and then a plateau phase, when all the hydroxide was removed from the surface. If the metal extraction continued indefinitely, this would indicate that the metal was now being extracted from the sulphide ore, and not the surface as expected from the theory of EDTA usage, and/or that the effect of gangue was too large for the successful application of the method.

The experimental program and dosages for the second level of tests are shown in Table 4-5 below. Note that tests using mild steel ore were also included in this level, so as to gain information at an early stage regarding differences in methodology that may be needed when treating ore milled with MS media.

Table 4-5: EDTA background tests, programme and results – level 2

Test No:	EDTA dosage (ul)	Metal abstracted (mg extracted/ g mineral) (x 10 ³)		
		Copper	Nickel	Iron
STD 1080	1080	0.2	0.3	ND
MS 1080	1080	0.1	0.4	19
STD 10800	10800	1.3	4.9	139
MS 10800	10800	1.2	3.3	257
STD 21600	21600	2.3	3.9	105
STD 54000	54000	1.5	3.9	108
Absolute ERROR (%)⁴		7	13	4

ND – Not detectable

Results for the second level of tests, shown as extraction curves for copper, nickel and iron are shown in Figure 4-3, Figure 4-4 and Figure 4-5 respectively.

A further 2 dosages were tested so as to maximise the range of dosages studied. In this regard, tests were conducted using dosages of 21600 ul and 5400 ul on samples milled with stainless steel media.

In Figure 4-3, Figure 4-4 and Figure 4-5 below, the results for all the dosage level tests shown in above presented graphically. Comparison with the theoretical curve indicates an acceptable similarity, all three curves having a tail end that forms a plateau, indicating the lack of further metal extraction irrespective of increasing EDTA concentration (with the copper result showing signs of some anomaly).

⁴ See "Appendix F" for further information regarding the calculation of standard deviations and absolute errors for EDTA complexation tests.

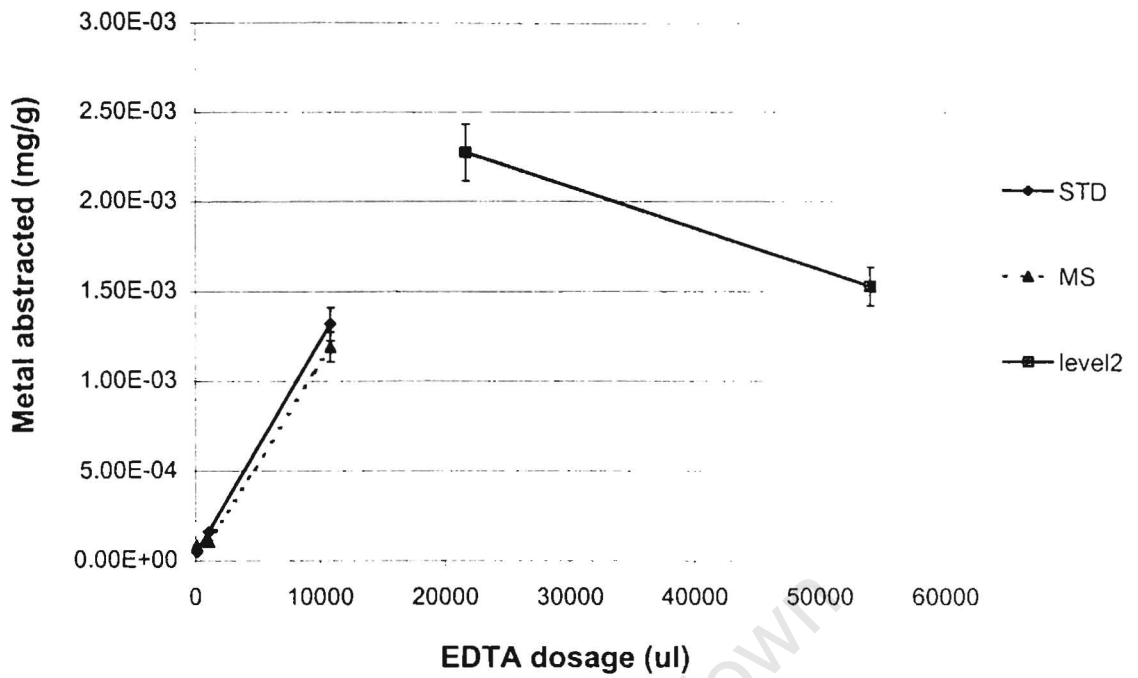


Figure 4-3: Copper extracted as a function of varying EDTA dosage - level 2

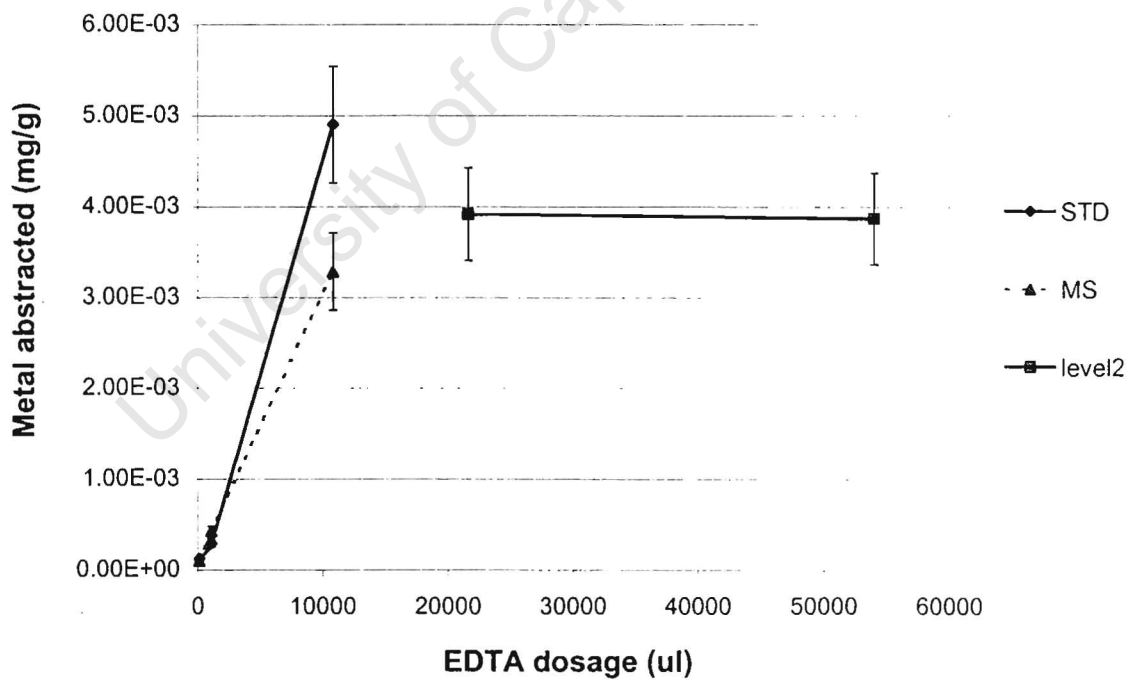


Figure 4-4: Nickel extracted as a function of varying EDTA dosage - level 2

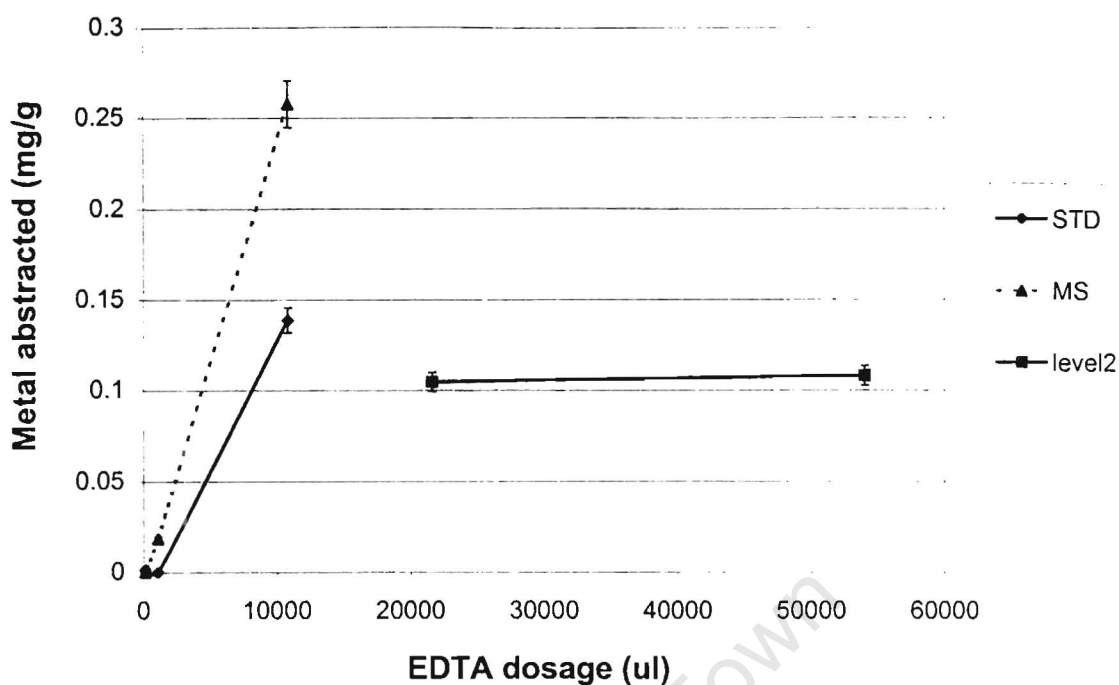


Figure 4-5: Iron extracted as a function of varying EDTA dosage - level 2

As can be seen in Figure 4-3, Figure 4-4 and Figure 4-5, the metal extraction increases proportionally to EDTA dosage initially, however, it eventually levels out independent of EDTA dosage. This result is extremely important, since it indicates that the technique for metal hydroxide - EDTA complexation is applicable to this complex sulphide PGM ore at high enough EDTA concentrations, without stripping the sulphide metal itself. At this stage however, it is unknown, whether this high concentration has any negative effects on the rest of the system (i.e. on the other reagents and reactions occurring within the system, such as the relationships between the collector, CuSO_4 activator and the mineral).

In any event, with the aid of results thus far, one can now choose an appropriate EDTA dosage level for use in testwork. For ease of handling, and to minimise consumption of reagent, a dosage of 20 000 μl was chosen for use in all further EDTA testwork.

4.3.3. Experimental Programme

Table 4-6 shows the experimental programme devised to answer some of the questions related to mineral surface oxidation, and the effect of milling media as outlined in section 2.7-Research Objectives:

Table 4-6: Experimental programme for EDTA metal extraction

Milling Media	Test Code	ORE (g)	gmols SIBX	gmols Cu	[SIBX:Cu] ratio	Gas added
Stainless steel	S1	94	1.48E-05	0.74E-05	2:1	None
	SN	101	1.59E-05	0.79E-05	2:1	N ₂
	SS base	94	1.48E-05	-	SIBX only	None
Mild steel	M1	94	1.48E-05	0.74E-05	2:1	None
	MN	89	1.40E-05	0.70E-05	2:1	N ₂
	MS base	93	1.46E-05	-	SIBX only	None

The results from the above EDTA metal extraction experiments are discussed in subsequent sections and presented in Table 4-7 below.

Table 4-7: Total metal extracted by EDTA from Merenksy ore under test conditions

Milling Media	Test Code	mg Fe/g	mg Cu/g	mg Ni/g
Stainless steel	S1	0.050	0.0024	0.0028
	SN	0.044	0.0022	0.0021
	SS base	0.046	0.0014	0.0032
Mild steel	M1	0.48	0.0019	0.0053
	MN	0.50	0.0013	0.0025
	MS base	0.44	0.0009	0.0039

Firstly, the reproducibility of the tests are discussed, followed by the results for the tests conducted with ore milled with SS media. The results are discussed in terms of the three metal elements analysed for, that is, Ni, Cu and Fe. The results of tests using ore milled with MS media then follow, and are presented in the same format. Finally, a summary of the main points from the EDTA extraction experiments is presented.

4.3.4. Reproducibility

The experiments conducted during the second level of EDTA experiments (See Table 4-5 above) were done in duplicate. This enabled a calculation of the standard deviation and % error for each type of metals analysis (with varying EDTA dosage, see Appendix F for more details). It was assumed that this error was consistent and applicable to the whole data set using the same experimental technique. The values for absolute error (%) for each metal species can be found in Table 4-5. As can be seen, the copper and nickel values have high associated errors.

4.3.5. SS Milling Media – EDTA Results

The results for nickel, copper and iron extracted by the EDTA – metal ion complexation technique, for tests using ore milled with stainless steel media, is presented and commented on below.

4.3.5.1. Nickel Results

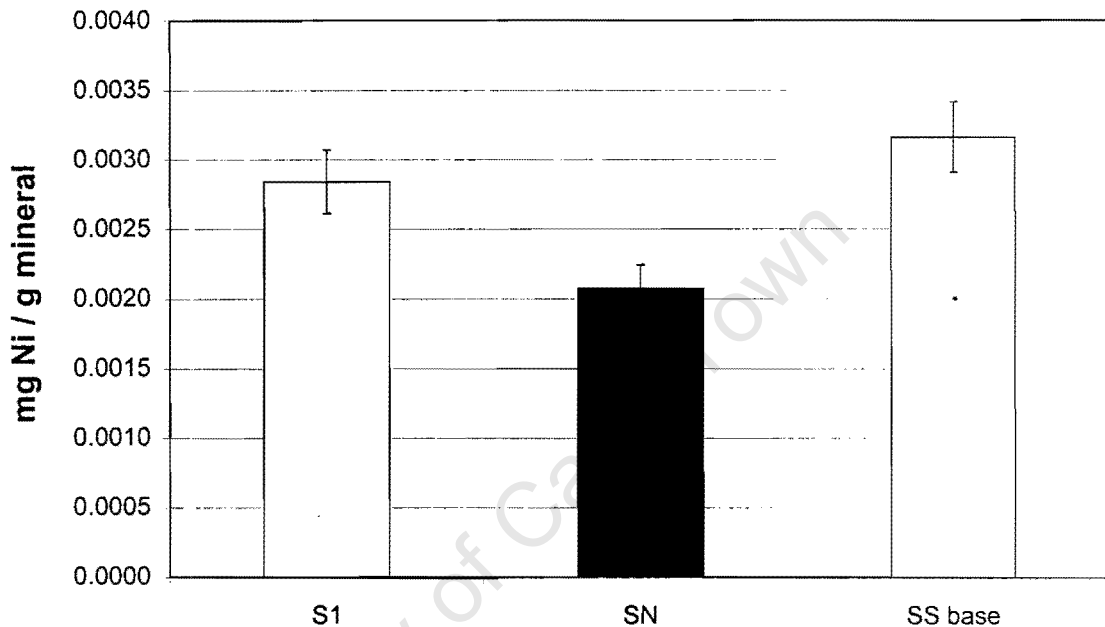


Figure 4-6: Total nickel extracted by EDTA after milling with SS media under different test conditions

Figure 4-6 shows the levels of nickel metal extracted by EDTA for tests using ore milled with stainless steel milling media. A considerable amount of nickel is extracted for the baseline case (ore and EDTA alone; SS base), implying that the surface of the mineral has already undergone some oxidation prior to the addition of any reagents, specifically the pentlandite particles (major nickel contributors in this ore). This is accounted for by the fact that the mineral has been handled and exposed to the atmosphere for periods of up to 2 hrs before freezing and storage of the sample takes place, as well as the oxidation that may occur during the experimental procedure (milling and subsequent handling).

The test with nitrogen shows a decrease in the level of surface oxide metal products removed. This suggests that the nitrogen slows down the rate of oxidation (and thus the level of oxides extracted after conditioning). It seems unlikely, however, that this slight decrease alone is the cause for the large

differences observed in flotation behaviour in previous testwork. It is most likely a combination of this and other factors (viz., the effect of nitrogen on the copper-xanthate reaction which we have previously demonstrated).

4.3.5.2. Copper Results

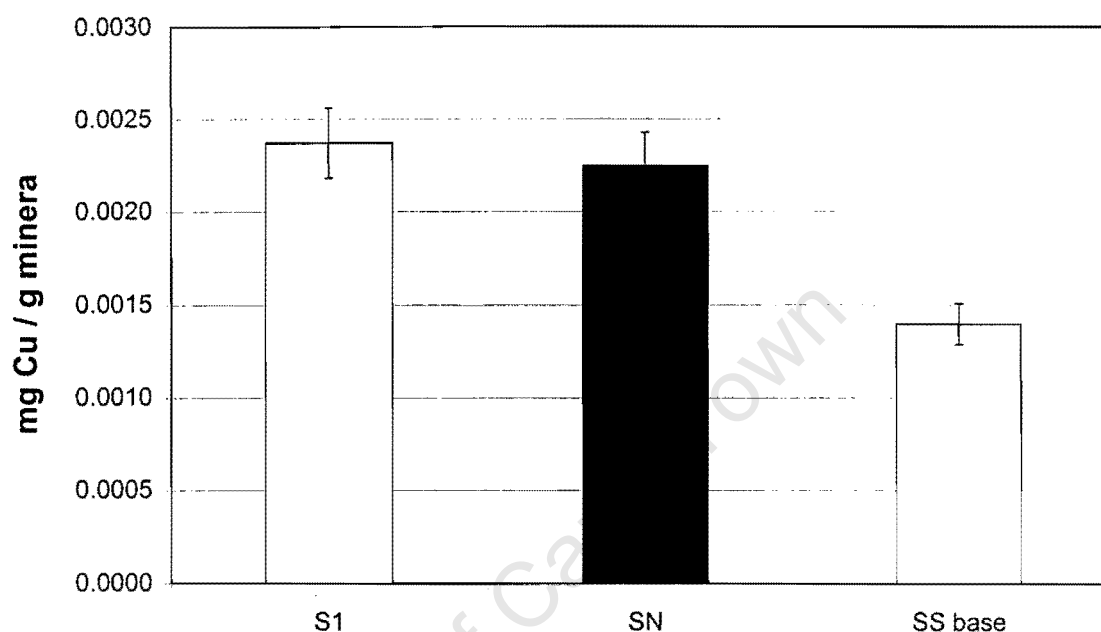


Figure 4-7: Total copper extracted by EDTA after milling with SS media under different test conditions

Figure 4-7 presents the levels of copper metal extracted by EDTA for tests milled in stainless steel milling media. As observed with the nickel in section 4.3.5.1 above, copper is extracted for the baseline case, and it is reasonable to assume that the ore possesses a certain amount of oxidised material after handling and sample preparation.

Comparing the tests with copper sulphate activator added (SN and S1) to that without (SS base), it can be noted that experiments with activator added result in a higher level of copper removed by complexation with EDTA. At first glance, this may seem to be an expected result, since more copper added should result in more copper removed, but it is important to keep in mind that we are attempting to extract the copper present as a hydroxide on the mineral surface, and not that present in any other form in solution. The results in Figure 4-7 indicate quite a large difference between the tests with copper sulphate added and that of the baseline case with no reagents added, and it may be possible that copper

extraction from a source other than the minerals' surface is occurring. In the context of the system, no excess copper is added, and so all copper added to the system, will complex with the xanthate and should be in the Cu-X form. In this light, such a large increase in copper abstracted could possibly imply that the large dosages of EDTA have a side effect; that of breaking up the Cu-X complex! In this regard, further tests with varying dosages of copper sulphate were conducted, together with a copper balance on the results. Details on these experiments can be found in Appendix C. The results for these tests with SS milled feed conclude that between 55 % and 70 % of the copper added to the system is removed by EDTA. Furthermore, the results of residual xanthate experiments (see section 4.2.3 above) calculate that the xanthate to copper reaction ratio is 1:1.8, implying that the copper *is* reacting with the xanthate, and that only a small percentage is not available for reaction (the decrease in ratio from 2 to 1.8). This small percentage in no way can account for the large amounts of copper removed, and the implication from this is that EDTA is probably breaking down the Cu-X complex. This conclusion places a serious hamper on work attempting to gain insight into the quantity and form of cupric hydroxides, in the presence of xanthate, using techniques based on EDTA complexation, at the current dosage.

With regard to the effect of nitrogen, the marginal differences that lie within statistical boundaries indicate that the nitrogen has no effect on the level of hydroxides removed. It may be more likely, however, that the effect discussed above (EDTA break-up of Cu-X) clouds the possibility of observing any differences regarding the level of hydroxides for the copper metal in general.

4.3.5.3. Iron Results

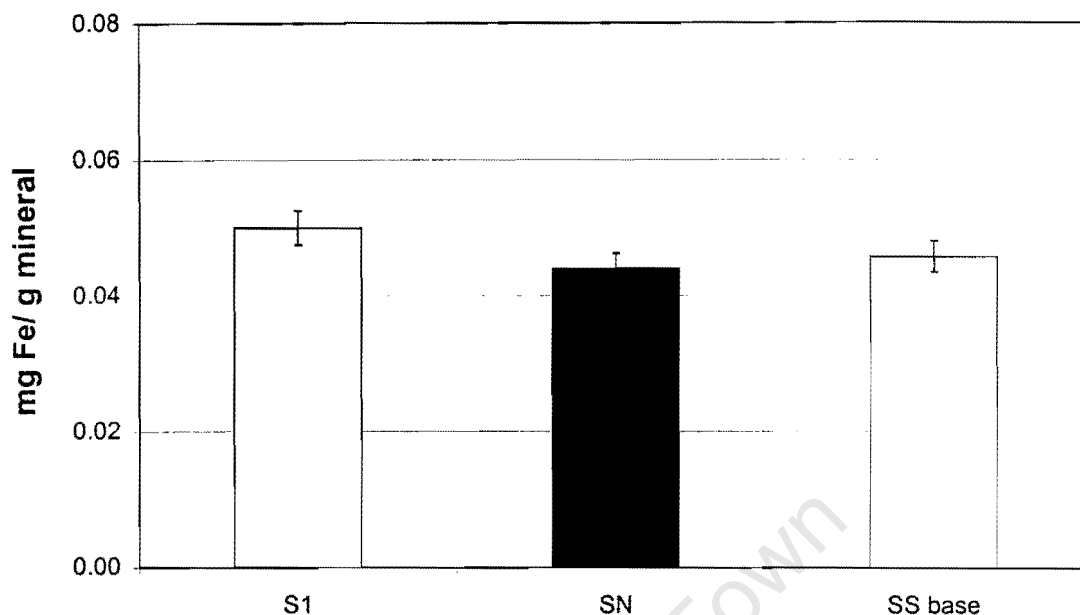


Figure 4-8: Total iron extracted by EDTA after milling with SS media under different test conditions

Figure 4-8 presents the levels of iron metal extracted by EDTA for tests milled in stainless steel milling media. As observed with both the nickel and copper, the ore is already oxidised and a fair amount of iron is complexed and removed by the EDTA for the baseline case.

The effect of nitrogen on hydroxide level is marginal and only weakly significant based on the observed standard deviation, and no conclusive proof of any interaction between hydroxide level and nitrogen conditioning can be demonstrated. Visually, however, we note that the test with nitrogen gas added resulted in the lowest level of hydroxides removed.

4.3.6. MS Milling Media – EDTA Results

The results for nickel, copper and iron extracted by the EDTA – metal ion complexation technique for tests using ore milled with mild steel media is presented and discussed below.

4.3.6.1. Nickel Results

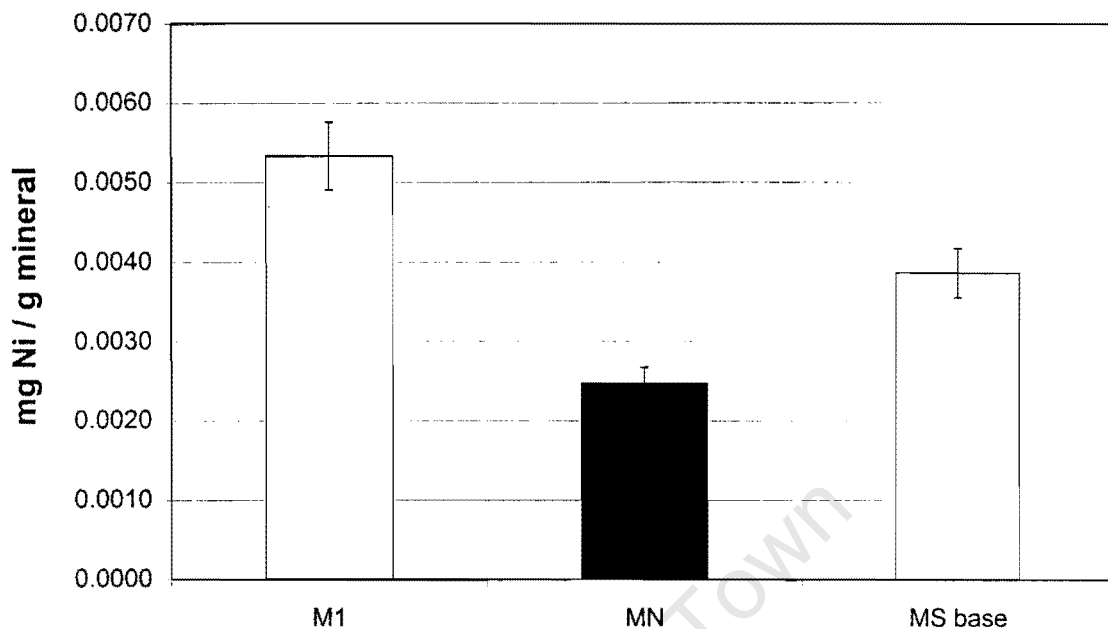


Figure 4-9: Total nickel extracted by EDTA after milling with MS media under different test conditions

Figure 4-9 presents the levels of nickel metal extracted by EDTA for ore milled with mild steel milling media. Once again, the baseline case shows a fair degree of oxidation, probably resulting from exposure during handling.

A general comparison with the stainless steel milled counterpart (see Figure 4-6 above) seems to indicate that the level of removed oxidised surface products are greater with mild steel milling than with stainless steel milling. It is not known why this should be so.

The test with nitrogen showed decreased levels of surface hydroxides relative to that without nitrogen. The reduction of surface hydroxides in the presence of nitrogen may be explained by a lowering of surface oxidation, however, the level of oxygen after mild steel milling is known to be very low in any event, so this is questionable.

4.3.6.2. Copper Results

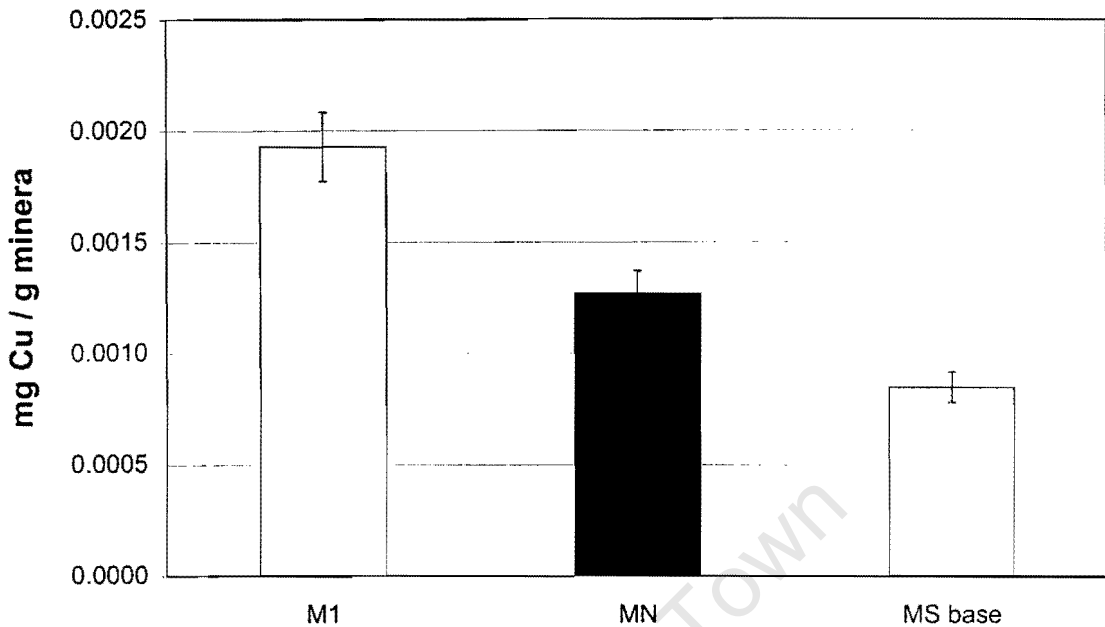


Figure 4-10: Total copper extracted by EDTA after milling with MS media under different test conditions

Figure 4-10 presents the levels of copper metal extracted by EDTA for ore milled with mild steel milling media. Once again, the baseline case shows a degree of oxidation, probably resulting from exposure during handling.

The degree of oxidation of the baseline case is, however, lower for mild steel than when compared to that observed during stainless steel milling (see Figure 4-7 above). Seemingly, the copper mineral is more protected from oxidation in the case of mild steel milling, and this may be a consequence of the large amounts of Fe present in the system (see 4.3.6.3 below) which oxidise at a rapid rate consuming all available oxygen in the system, hindering the further oxidation of copper mineral. On the other hand, it may be that the high level of iron consumes all the EDTA during the extraction process, leaving little available for removal of the copper hydroxides. This may be likely, but is improbable since the dosage of EDTA used is already very high. More importantly, however, we have established that this EDTA dosage causes misleading results when assessing copper minerals due to break up of the Cu-X complex.

The test with nitrogen displays lower levels of surface products removed relative to the test not conditioned in nitrogen (M1 vs. MN), and noting that the masking

effect of Cu-X breakup should be equal in both these instances, the results indicate that the level of oxidation in this instance is lowered to some extent.

4.3.6.3. Iron Results

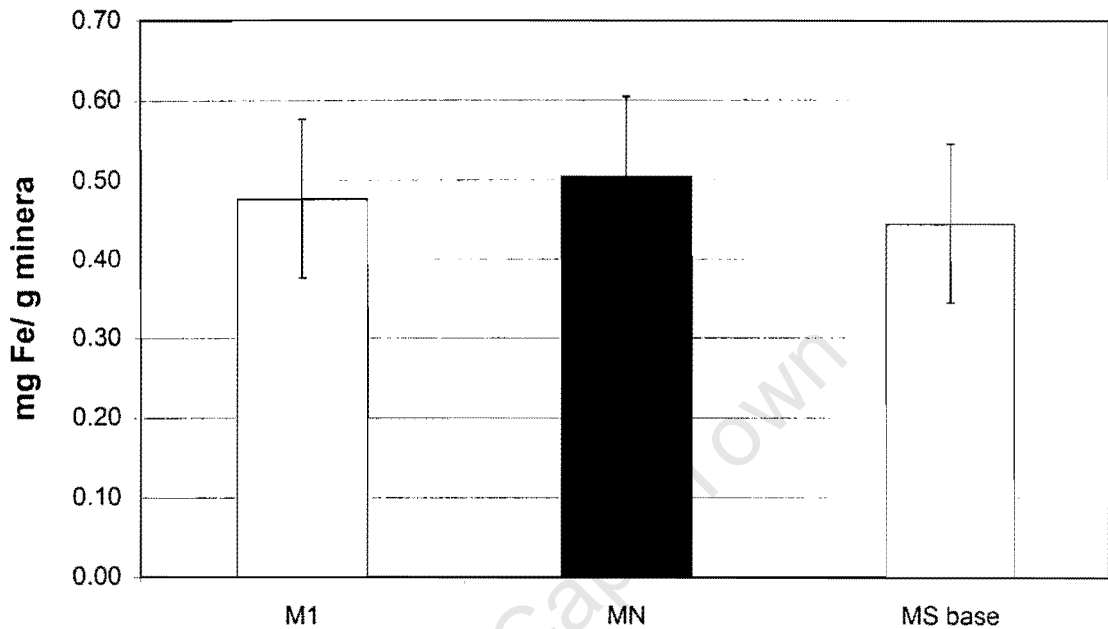


Figure 4-11: Total iron extracted by EDTA after milling with MS media under different test conditions

Figure 4-11 presents the levels of iron metal extracted by EDTA for ore milled with mild steel milling media.

The thing to note in this instance is the difference in scales when comparing these results to those of the stainless steel case (see Figure 4-8 above). The first observation is thus as follows; During mild steel milling, the amount of iron in solution is more than tenfold that during stainless steel milling! This implies a major difference in the pulp chemistry and controlling reactions between the two systems, and is probably one of the main contributors to the differences observed in flotation experiments using stainless steel milling and those employing mild steel milling. The large quantities of ferrous ion also explain the low levels of oxygen present in a pulp created from ore milled using mild steel media.

The above conclusion is the most important, and the only one that can be confidently stated due to the high standard deviation present in the results.

4.3.7. Summary – Measurement of Surface Hydroxides by EDTA Complexation

The major findings of the EDTA metal hydroxide abstraction testwork can be summarised as follows:

1. The developed technique for metal hydroxide - EDTA complexation is applicable to this complex sulphide pgm ore, but at only at high EDTA concentrations due to the high gangue to mineral ratio. The drawback to this is the probable breakdown of activator – collector (Cu-X) complex from the pulp, resulting in the inability to accurately monitor the level of copper hydroxides on the mineral surface.
2. For tests employing mild steel milling, the amount of iron extracted was more than tenfold that extracted for tests employing stainless steel milling
3. For stainless steel milled ore, nitrogen conditioning resulted in a lowering of the level of metal (hydroxide) products removed, especially in the case of nickel. The large standard deviations, however, results in a low confidence level being associated to this result .
4. For mild steel milled ore, the use of nitrogen resulted in decreased levels of surface hydroxides for both nickel and copper metals (the iron results being inconclusive).
5. For mild steel milled ore, a baseline comparison with stainless steel milled ore showed that nickel levels extracted after mild steel milling were higher than the stainless steel case while those for copper were lower.

5. DISCUSSION OF RESULTS

The purpose of this section is to relate the results from this investigation with those obtained by other researchers. Additionally, we will attempt to elucidate the mechanisms at work with the aid of the complementary investigations.

The chapter starts out with a summary of the key findings. Possible mechanisms that may be occurring are then suggested (as identified from the literature and original hypotheses) and categorised with their supporting evidence.

Finally, a detailed discussion of each hypothesis with relation to the observed results and a probing of the literature to elucidate mechanisms follows.

5.1. Summary of Key Findings for All Results - Batch Flotation and Complimentary Studies

In addition to batch flotation and pulp chemistry measurements, two complimentary studies were conducted. These were carried out so as to elucidate the mechanisms responsible for flotation response in the presence of nitrogen, and to gain better insight into the system under study. This section highlights the KEY findings from all the experimental work.

In the batch flotation of ore milled with stainless steel media the use of nitrogen gas during *conditioning* resulted in a recovery benefit for nickel. Additionally, the use of nitrogen in *flotation* resulted in increased mass pulls for the majority of tests. When *both* nitrogen conditioning and flotation was employed in the flotation step, a general depression of all sulphides was observed. In the batch flotation of ore milled with mild steel media, a reducing environment characterised by high mass pulls but correspondingly low grades resulted.

The pulp chemistry measurements showed that the use of nitrogen resulted in the creation of less oxidising conditions, independent of the point of application (i.e. during conditioning, vs. during flotation). This was characterised by the measurement of lower DO and ORP values. Tests milled using mild steel media resulted in lower ORP's and DO's after milling, than corresponding tests milled in stainless steel media. This indicated the presence of more reducing conditions. The use of nitrogen in these instances, was consistent, and resulted in further reductions in the ORP and DO levels. When air was used as the flotation gas (STD and NA tests), the observed ORP limits were found to be acceptable for

dithiolate formation. With the use of nitrogen during flotation, however, the potential was dropped to levels at which dithiolate formation is unlikely.

The study of residual xanthate measurements showed that copper and xanthate react in a stoichiometric ratio of 1:2 respectively when no other components are present in the system. The addition of ore caused the stoichiometric ratio to decrease to 1:1.8. A consistent feature of nitrogen addition (in the presence of ore) during conditioning was a substantial increase in measured residual xanthate. No significant change in measured residual xanthate levels were found between tests using aged ore and those employing fresh ore. Finally, little or no interaction was found to exist between Fe^{++} (added as FeSO_4) and Xanthate at the conditions under current investigation.

The study of mineral surface oxidation as a result of the EDTA complexation measurements indicated that for stainless steel milled ore, nitrogen conditioning resulted in a lowering of the level of surface oxide metal products removed, especially in the case of nickel. Furthermore, during tests employing mild steel milling media, the amount of iron extracted was more than tenfold that extracted for tests employing stainless steel milling media.

5.2. Mechanisms in Support of the Key Findings

One of the expected outcomes related to the use of nitrogen during batch flotation was a possible benefit in flotation performance. The mechanism attributable to this was a reduction in mineral surface oxidation. Simultaneously, however, the effect of nitrogen on other issues such as galvanic interactions, mineral-collector interaction and froth effects was also flagged as relevant and were noted as having possible negative outcomes in certain instances (i.e., reduced collector - mineral oxidation). In summary, the results, both positive and negative, were identified as being attributable to one or more of the following mechanisms:

- Reduced mineral oxidation as a result of nitrogen conditioning leading to improved flotation.
- Reduction in mineral surface - collector interaction caused by hindered collector oxidation as a result of nitrogen addition, leading to poor flotation.

- Nitrogen influencing the mineral surface - collector - activator (copper sulphate) interaction.
- Nitrogen having a direct or indirect effect on the nature of the froth chemistry and mobility as a consequence of galvanic interactions or the type of milling media used.

In the next section, we will investigate the mechanisms identified above in greater detail and show that the results of the complimentary investigations confer with these proposed mechanisms. Additionally, we compare the findings obtained in this investigation with those of other researchers.

5.3. A Discussion of the Role of Nitrogen with Regard to the Proposed Hypotheses

Now that we have briefly laid out our thinking with regards to the role of nitrogen (c.f. 5.2 above), we move forward by attempting to criticise our hypotheses and thinking with regard to the classical arguments made for the behaviour of nitrogen as found in the literature.

This discussion starts off with an attempt at explaining the role of nitrogen on mineral surface oxidation and the mineral – collector – activator relationship. The complexity of a different milling media is then introduced into the discussion, together with the considerations of the changes in mechanisms of the pulp phase and any subsequent effects on the froth phase.

5.3.1. The Effect of Nitrogen on Mineral Surface Oxidation and Mineral - Collector – Activator Interactions

The argument for reduced mineral oxidation as the reason for improved performance stems from two possible avenues.

Firstly, mineral oxidation leads to formation of hydrophilic species that inhibit flotability at large. These can be in the form of ions from the pulp solution oxidising and precipitating on the mineral surface, or direct oxidation reactions at the mineral surface. When dealing with complex sulphide systems, competition between the different minerals will exist in terms of their natural potential for oxygen activity. Rand (1977) studied the rate of reduction of oxygen on different

minerals. The rate of reduction in this case can be seen as the key variable that determines the extent to which the mineral will oxidise relative to other minerals in the system. Rand found that the rate on a pyrrhotite surface was very much faster than on pentlandite. Hence, the pentlandite undergoes oxidation at a much slower rate, which implies reduced hydrophilic species and thus probable improved flotability. If this mechanism were to be responsible for the observations noted in practice with this system, then differences in the levels of surface hydroxides on pentlandite and pyrrhotite should be observed⁵.

Although the introduction of nitrogen has been portrayed above as beneficial from the point of view of reduced mineral surface oxidation, it is important to point out that it can simultaneously adversely affect flotation mechanisms. Galvanic interaction mechanisms where certain minerals are 'cathodically protected' from oxidation by other coupled minerals could be one of the areas of negative impact. The conditions essential for the occurrence of galvanic interactions are firstly, physical contact between the different sulphide minerals (in slurries, milling, or in locked particles), and secondly, the presence of oxygen for the cathodic reduction reaction (and subsequent anodic oxidation of the sulphide mineral). In this regard, the galvanic protection mechanism is in operation under nitrogen free flotation conditions. When nitrogen is employed, however, the lack of oxygen would hinder galvanic interactions.

Considering the two arguments above, it is apparent that a contradiction exists regarding the effect of nitrogen in terms of decreasing levels of oxidation on pentlandite relative to pyrrhotite. On one hand, clearly the removal of oxygen will decrease oxidation levels for all minerals present, and due to the difference in oxidation rates, any superficial oxidation that occurs will occur to a greater extent on the pyrrhotite than the pentlandite. In this instance, the pentlandite would be more shielded from harmful oxide / hydroxyl species relative to the pyrrhotite. At the same time however, the 'cathodic protection' mechanism put in place by galvanic contact is hindered by the lack of oxygen in the system.

At this point it becomes clear that establishing relative magnitudes of the galvanic effect relative to the other effects caused by oxygen removal is the key to identifying which of the proposed mechanisms are dominant in this system.

⁵ The hydroxide levels on individual minerals can only be accurately measured with (expensive) direct measurement techniques i.e. FTIR (Fourier Transform Infrared Spectroscopy) or TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy), however, the value of such experiments can easily be gauged beforehand with inexpensive, indirect measurement techniques (i.e. EDTA metal hydroxide complexation)

Clearly, the best way to ascertain the effect of nitrogen on mineral surface oxidation would be to study the mineral surface under test conditions. In this regard, the implementation of a procedure that allows the measurement of the level of surface oxidation products is desirable. The methodology using EDTA devised during this investigation and developed specifically for the complex sulphide ore used in this study was used to gain evidence for changes in mineral oxidation, either as a product of galvanic effects or nitrogen conditioning. Initially, the effect of nitrogen on flotation was thought to be as a result of either a decrease in the level of surface oxidation, or by its effect on the collector-mineral-activator reactions.

The EDTA extraction tests show that although the tests with nitrogen show little difference in comparison to those without nitrogen, they *do* result in the lowest level of surface oxide metal products removed. This suggests that the nitrogen slows down the rate of oxidation and thus the level of oxides produced. It seems unlikely, however, that this slight decrease alone is the cause for the large differences observed in flotation behaviour in previous testwork. It is most likely a combination of this and other factors such as interference in collector – activator interaction that finally contribute to the observed final flotation response.

Similarly, when assessing nitrogen's effect on the mineral surface - collector – activator interaction, the obvious procedure would be to investigate the reaction between these 3 components under test conditions (the ore, the collector and copper sulphate). Any observed changes in these reaction mechanisms under test conditions may indicate an area for further investigation. In this regard, the measurement of residual xanthate levels by UV provide an easy way of assessing changes in collector – activator – mineral interaction, should any be occurring.

The results of these tests lead to the following observations.

The effect of nitrogen on the Cu - X reaction was a substantial increase in the measured level of residual xanthate. This directly implies that the presence of nitrogen in some way affects the Cu - X reaction, and that possibly both the mechanism of the Cu - X reaction, and form of the copper may be different in this scenario. This has significant implications in identifying which mechanism is responsible for the change in flotation response, since it implies that the collector – activator mechanism is altered by the presence of nitrogen.

No significant change in residual xanthate between tests using aged ore and those employing fresh ore was found implying that the surface available for collector adsorption did not change significantly with ageing, or that the interaction of the copper with the xanthate overshadows any subtle difference in collector adsorption.

The 1:1.8 reaction ratio between collector and activator noted for tests employing normal ore was once again observed for the tests using aged ore.

Furthermore, nitrogen conditioning once again resulted in higher levels of residual xanthate relative to non - nitrogenated conditioning (when using aged ore). It is important to note, however, that this does not necessarily imply a surplus of xanthate available for the reaction with the mineral, since excess copper always results in a zero residual of xanthate, with or without nitrogen. It merely serves to indicate a possible change in the mechanism at a microscopic level that is otherwise not visible at the macroscopic level of the flotation tests.

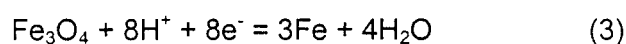
5.3.2. Changes in Milling Media and Its Effect on Measured System Performance

5.3.2.1. The Effect of Media Changes on Pulp Chemistry Profiles

A short discourse on the significance of variations in the pulp chemistry profiles measured during the flotation tests is presented below. Samples of the profiles discussed can be found in section 4.1.1 and 4.1.2. Much of the discussion below is intuitive, but is nevertheless presented for the sake of completeness.

- Variations in ORP:

The primary observation here is a more reducing environment for ore milled with mild steel media relative to that milled in stainless steel media. This is directly linked to the reactions of ferrous ions released during mild steel milling. The reactions are any one of the following (Forssberg and Subrahmanyam, 1993):



Consumption of electrons in these reactions causes the shift to more reducing conditions in the pulp.

ORP changes also occur on reagent addition. Positive ions (Cu^{++} from activator) cause the system to move to a more oxidising scenario, while the negative xanthate ions cause a sharp drop in the ORP, indicating a shift to more reducing conditions in the pulp. It is noticeable however, that in tests where the ore was milled using mild steel media, the magnitude of ORP change on copper addition (visible as a spike at 5 minutes) is not as pronounced as in the case of stainless steel milling. This may be because the system is already acting as a positive ion reserve (Fe ions), and additional Cu^{++} ions marginally affect the balance and there is correspondingly little shift in electron activity relative to the stainless steel milling media case.

ORP's decrease with the use of nitrogen either as a flotation and / or conditioning gas. This is primarily as a result of purging of oxygen from the system, resulting in a shift to a more reducing (less oxidising) environment.

- Variations in DO:

DO levels for pulps milled in stainless steel and those milled in mild steel have intrinsically different pulp chemical regimes and this is manifested in the measured differences in DO levels. Pulps that have been milled in mild steel media showed characteristically low DO levels. This is linked to the reactions (1), (2) and (3) above. Oxygen acts as the electron donor in these reactions, and so the diminishing of electrons is directly proportional to the diminishing of dissolved oxygen in the pulp.

Nitrogen addition has the expected effect of lowering the DO level as oxygen is purged from the system. Once nitrogen addition stops, the stirred pulp usually re-attains its previous equilibrium value.

- Variations in pH and Temperature:

There are no observed differences between either the temperature or pH of ore milled with mild steel media and that milled in stainless steel media. This is expected. The natural pH of the pulp was basic and approximately 9, and the Cu and Fe ions are most likely to be present in their hydroxide phases at this pH.

5.3.2.2. Metallurgical Responses to Milling in Mild Steel

Changes in milling media, sometimes coupled with changes in conditioning and / or flotation gas type, resulted in different flotation responses (see c.f. 3.4). The key differences in flotation with respect to the change between mild steel and stainless media are as follows;

1. The mass pull and recoveries of metal sulphides were higher for flotation tests using mild steel milling media. Grades were correspondingly lower.
2. The resultant pulp environment is more reducing with mild steel milling, corresponding to lower DO and ORP levels.
3. A highly stable froth zone for flotation tests employing ore milled with mild steel milling media.
4. Finally, when adding nitrogen during *both* conditioning and flotation, the only metal recovery *not* detrimentally affected was nickel recovery for the test employing ore milled with mild steel media. This is contrary to the observed effect of employing nitrogen in *both* the conditioning and flotation steps, where, both in the case of mild steel and stainless steel milled ore flotation tests, these affected the copper, nickel and iron detrimentally (with the one exception for nickel mentioned above).

The observations numbered 1 to 3 above are to an extent intuitive, in terms of their accordance with the general principles laid out in the literature regarding the use of conventional grinding media (mild steel).

Firstly, the corrosion reactions during conventional grinding cause the release of ferrous / ferric ions into the pulp. At the natural alkaline pH of the pulp, these exist as iron hydroxides. In a reducing environment, the presence of these hydrophilic species can be detrimental to flotation performance if they coat the mineral surface (Forssberg, Subrahmanyam and Nilsson, 1993). In addition to this possible negative impact, these hydrophilic metal colloid species could play a dual role and help to stabilise the froth zone (Bikerman, 1996).

With this in mind, it is likely that the froth stabilisation observed is as a result of the high levels of ferrous hydroxides present in the pulp as a result of the corrosion reactions in the system. This more stable froth results in higher carryover, and ultimately higher recovery of bulk sulphides. The stable froth, being unselective in nature, simultaneously carries over higher quantities of

gangue material as well. This would explain the high recovery and low grade observed.

Secondly, the reducing environment characterised by the low DO and ORP levels serves to reduce mineral surface oxidation and the formation of surface hydrophilic species, which may aid collector – mineral interaction and thus improve flotability. Conversely, it could be argued that this same reducing environment adversely affects collector oxidation by virtue of its lowering of the solution pulp potential, possibly to levels below the critical limit required for dithiolate formation. If the presence of dithiolate as a hydrophobic collecting species is essential to flotation, then clearly flotation will be adversely affected.

Judging from the results obtained and outlined in points 1 - 3, the dominant reactions from all the competing effects discussed above appear to be those that favour high recoveries, and low grades, without any detrimental effect to any particular sulphide mineral (purely for the case of a milling media change).

The reducing action of mild steel milling may indeed aid collector – mineral interaction (by limiting oxidation), and the subsequent flotation process, but at this stage further evidence is required before any concrete statement regarding this can be made. It can be said though, that the reducing environment provided by the milling media alone is not enough to harm the mineral – collector interaction such that poor recoveries are observed. The use of nitrogen, however, by means of its total purging of oxygen from the system prior to collector addition, does indeed affect dithiolate formation. Rao and Finch (1990) confirmed this in their study on the oxidation and adsorption of xanthates in the presence of nitrogen and / or cations. An important finding of their work is the lack of dixanthogen in solution in the presence of nitrogen. When an oxidising ion like Cu^{++} is also present in solution, dixanthogen forms, however, none is found on the mineral surface in the presence of nitrogen. An equally significant observation was a large decrease in xanthate uptake by pyrrhotite in the presence of nitrogen. (This has a significant implication to flotation processes where pyrrhotite rejection is the desired objective for separation from the valuable mineral.)

In the present study, it would seem that the results indicate that dithiolate formation, (or equivalent DO and ORP levels), is required for iron (pyrrhotite) and copper (chalcopyrite) recovery, but not necessarily for nickel (pentlandite) recovery. Spectrophotometric studies on the extracted mineral surface reaction products after reaction with xanthates have shown that the species present on

both chalcopyrite and pyrrhotite is dioxanthogen (Allison et.al. 1972), which conforms with the theory that nitrogen inhibits collector – mineral interaction, and thus hydrophobicity for these species.

Kelebek (1993) studied the effect of oxidation on the flotation behaviour of nickel-copper ores with similar results. The work carried out employed stainless steel media, but milling was carried out in an inert, reducing, nitrogen atmosphere. Indeed, many laboratory studies use this methodology to simulate conventional grinding conditions (without the added complexity of corrosion effects), i.e. mild steel milling. Flotation was carried out using both nitrogen and air, as was the case in the present thesis. The table below lists the metallurgical results of the flotation tests in terms of pentlandite, chalcopyrite and pyrrhotite recoveries.

Table 5-1: Pentlandite, chalcopyrite and pyrrhotite recoveries (Kelebek, 1993)

	Pentlandite Recovery %	Chalcopyrite Recovery %	Pyrrhotite Recovery %
SS / Nitrogen	60	26	10
SS / Air	62	77	26

For the chalcopyrite and pyrrhotite minerals, changing the pulp environment to more reducing conditions causes a sharp decrease in recovery, while at the same time showing little detriment to the pentlandite recovery, *as is observed in the present study.*

The ease of mineral flotability, which under normal conditions is Chalcopyrite > Pentlandite > Pyrrhotite, was changed to Pentlandite > Chalcopyrite > Pyrrhotite under oxygen-deficient conditions. This behaviour has been correlated to the catalytic activity of these minerals for oxygen reduction (Kelebek, 1993). Also, there is a significant difference between the catalytic activity of pentlandite and those of chalcopyrite and pyrrhotite. This is offered as the explanation for the observed flotation difference: i.e. due to high catalytic activity, pentlandite can develop hydrophobicity even under oxygen deficient conditions and float at low potentials, where dithiolate formation is unlikely, as is the case when flotation is with nitrogen. This may also indicate that the mechanism for pentlandite flotation is not dependent on oxygen acting as an electron acceptor.

In conclusion, we can say that regarding the effect of milling media, the effects observed are explainable and concur with those observed in past research. With

regard to certain observations, like froth stability and increased level of hydroxides, the complementary investigations involving the measurement of surface hydroxides by EDTA complexation resulted in evidence that corroborates our proposed explanation thus far.

During mild steel milling, the amount of iron in solution is more than tenfold that during stainless steel milling. This implies a major difference in the pulp chemistry and controlling reactions between the two systems, and is probably one of the main contributors to the differences observed in flotation experiments using stainless steel milling and those employing mild steel milling.

The large quantities of ferrous ion also explain the low levels of oxygen present in a pulp created from ore milled using mild steel media. Furthermore, it was proposed that if hydrophilic metal colloid species were present, in addition to their possible negative impact of coating the mineral surface, they could play a dual role and help to stabilise the froth zone (Bikerman, 1996), and lead to the high recoveries observed. Evidence of such large concentrations of hydroxides may be proof of this.

In answer to the question of why nitrogen does not benefit flotation performance when used in conjunction with mild steel milling media, we can then argue that the presence of large quantities of hydrophilic metal colloid species and the subsequent froth zone behavioural changes may lead to other effects that swamp out any subtle changes in the pulp zone. In other words, even though the levels of DO and ORP are similar, there are fundamental differences in the nature of the pulp chemistry that ultimately results in different flotation performance.

This demonstrates the importance of the froth zone in terms of its contribution to flotation performance (as observed in this study). The next section examines the froth zone in greater detail and presents an overview of the effects of milling media and galvanic interactions on this phase.

5.3.3. Froth Phase: Effect of Milling Media and Galvanic Interaction

The literature published on this topic is broadly divided into two opinions. Martin et.al. (1991) state that, in general, stainless steel or autogenous grinding leads to improved flotation of unactivated pyrrhotite, chalcopyrite and pentlandite. On the other hand, Van Deventer et.al. (1991,1993) showed that in the case of a complex sulphide, galvanic interactions caused by the presence of metallic iron in

a ceramic mill yielded a stable well drained froth resulting in high sulphur grades, while the absence of metallic iron produced a brittle froth with high recovery of iron and low sulfur grades. These contradictory results imply that the interaction between galvanic effects and froth behaviour is still unclear. Van Deventer et al (1998) point out that incorrect conclusions that are drawn in such instances are largely due to the fact that only pulp phase considerations are considered in the literature.

The general effect of media-mineral galvanic interaction is the enhanced formation of a stable coating of metal hydroxides which in turn inhibits flotation. An equally important effect of galvanic interaction between the mild steel media surface and the mineral's surface could be the significant lowering of the mineral's rest potential, which in turn inhibits the formation of dixanthogen (Deventer, 1998). Contact angle studies show that when dixanthogen is present, a highly hydrophobic surface results. Clearly, in the case of mineral - mineral separation, formation of a highly hydrophobic species on both minerals is detrimental to separation. From this point of view, rest potential control can be seen to be important to the eventual achievement of the desired separation. Most authors have measured rest potentials in laboratory environments and these cannot always be extrapolated to industrial flotation pulps. Rao et.al. (1976) observed that most sulphides had mixed potentials above X / X_2 couple at differing concentrations of potassium ethyl xanthate (PEX), while the mixed potential of the same minerals in contact with metallic iron were substantially lower than the X / X_2 redox couple. From this, it is probable, that the metal xanthate will form on sulphide minerals when they are in galvanic contact with mild steel. Alternatively, if these minerals are milled under semi-autogenous conditions, there is a high probability that dixanthogen will form on their surfaces. Consequently, low selectivity between the minerals will result and the froth will be loaded with highly hydrophobic particles. Harris (1982) and Dippenaar (1982, 1982) observed that very hydrophobic particles destroy froths. Furthermore, one particle can rupture numerous films, implying that only a few highly hydrophobic particles are needed for such a destabilisation process to occur. The milling media, therefore, not only has an effect on the pulp phase by way of pulp chemical interactions, but also has an indirect effect on the froth phase via its role in galvanic interaction.

Galvanic interactions can thus have a direct effect on the froth behaviour, as well as the pulp behaviour, and can simultaneously promote better collection in the

pulp phase, but result in poorer overall flotation performance. In this study, the preceding argument can be applied to explain the differences between mild steel and stainless steel milling from the viewpoint of froth performance. That is to say, that froth stability in the case of mild steel milling leads to high carryover of both metal and gangue, whereas in the case of stainless steel, the brittle, highly hydrophobic froth, causes drop-back of both valuable material and gangue to result in a lower carryover overall. In our case, for stainless steel milling, nitrogen was seen to affect mass pulls and so has a possible effect on the froth stability. Furthermore, for mild steel milling, a significant lowering of the minerals rest potential occurs as a result of galvanic interactions, which in turn inhibits the formation of dixanthogen. In this instance, the reduction of galvanic interaction by the addition of nitrogen implies a less hydrophobic mineral surface, which in turn implies a more stable froth (vs. highly hydrophobic particles in froth). In this regard, it is likely that nitrogen affects the nature of the froth indirectly by altering the galvanic interactions occurring in the pulp.

Another observation with regard to froth stability can be found in the statistical analysis of mass pulls. It is interesting to note that the standard deviations are of the same order of magnitude for both tests with mild steel and stainless steel milled ore (4.81 for SS vs. 4.77 for MS). The significance here is that the actual mass pulls for these two conditions differ by a factor of 2, the mild steel tests having a mass pull twice that of the stainless steel tests. In effect, the absolute relative deviation of the tests milled using mild steel ore is half of those milled using stainless steel ore. This seems to indicate that the mild steel system is somehow more stable with regard to froth flotation performance than the corresponding stainless steel milled case for this ore at the test conditions. Indeed, the tests measuring the level of surface hydroxide show evidence of a high level of iron which can possibly be corroborated with the increased froth stability.

5.3.3.1. Evidence for Galvanic Interactions

A feature of the occurrence of mineral-mineral galvanic interactions would be the oxidation of pyrrhotite preferentially over pentlandite for mild steel milling. Additionally, the occurrence of a mineral-media galvanic interaction would result in a higher level of surface hydroxides for mild steel milling (c.f. 2.5 The Mill Environment: Reactions). Verification of this hypothesis was impossible from batch flotation results, and tests measuring the level of surface hydroxides were

used to gain a better understanding in this regard. It was observed that for mild steel milling, the level of hydroxides on nickel were significantly higher than that observed for stainless steel milling. This verifies that the mineral-media galvanic interactions are occurring during mild steel milling, and that the data is inconclusive with regards to the existence of a galvanic protection mechanism.

Additionally, the use of nitrogen on pulp milled in mild steel media in the presence of collector and activator resulted in significantly lower levels of surface hydroxides removed by EDTA. This indicates that with the addition of nitrogen, the level of surface hydroxides on the pentlandite surface is decreased via displacement. It is possible that this could be as a result of enhanced collector-mineral interactions in the presence of nitrogen and subsequent displacement of loosely bonded hydroxy coatings by MX species. Additionally, if galvanic interactions continue to occur in the pulp after milling, and during conditioning, it can be argued that the nitrogen addition serves to hinder galvanic interactions and therefore decrease the level of surface hydroxides present on the minerals.

6. CONCLUDING REMARKS

A number of important observations have been made with respect to the role of nitrogen on flotation performance of PGM sulphide minerals, on mineral surface oxidation of major sulphide minerals, and on the collector – mineral – activator relationship.

Nitrogen gas addition during the conditioning stage of flotation leads to recovery benefits for the nickel minerals (pentlandite), with no benefit to copper (chalcopyrite) and iron (pyrrhotite), when stainless steel media is used in the preparation of pulp during the milling stage. Previous studies suggested that the improvement in nickel recovery could be due to reduction of hydrophilic species on the mineral surface, as a consequence of the low ORP and DO levels associated with nitrogen addition. Tests (ex-situ) measuring the level of surface hydroxides under simulated test conditions found that a lower level of surface hydroxides were removed from the nickel minerals' surface when the pulp was conditioned with nitrogen. At the same time, however, the magnitude of the change in the level of surface hydroxides was not deemed sufficient to be solely responsible for the observed recovery increase. The results of further investigations on the role of nitrogen on collector – activator – mineral relationships indicated that the presence of nitrogen in conditioning significantly decreased the stoichiometric ratio of the xanthate to copper reaction. This is an important observation, and implies a fundamental change in the reaction mechanism between the mineral and collector in the presence of copper sulphate activator during nitrogen conditioning.

Nitrogen used in BOTH the conditioning and flotation stages reduces the recovery of copper (chalcopyrite) and iron (pyrrhotite), but NOT nickel (pentlandite). This indicates that dithiolate formation, (or equivalent DO and ORP levels), is required for iron (pyrrhotite) and copper (chalcopyrite) recovery, but not necessarily for nickel (pentlandite) recovery. This is supported by Kelebek (1993) who showed similar trends for flotation results (see literature review). In this instance, pentlandite's ability to develop hydrophobicity under oxygen free conditions is cited as the reason for the observed behaviour of nickel recoveries being unaffected by the addition of nitrogen during *both* conditioning and flotation.

Furthermore, the literature suggests that dixanthogen is the active collector for chalcopyrite (Allison, 1972 and Leja, 1962), and pyrrhotite (Allison, 1972) minerals, which confers with the hypothesis that nitrogen blanketing of the flotation system results in hindered dithiolate formation, and thus reduced performance of minerals dependant on it.

Nitrogen conditioning does not benefit flotation performance when used in conjunction with mild steel milling media. It is likely that the low ORP and DO synonymous with mild steel milling have already covered any benefits that nitrogen addition presents by resulting in similar pulp chemical conditions. Furthermore, tests measuring the level of ferrous ions indicate that there is tenfold more Fe present as hydroxides after mild steel milling compared to after stainless steel milling, indicating that the pulp chemistry is significantly different when mild steel media is employed. The subsequent froth stabilisation that occurs as a direct result of these hydroxy species may lead to other effects that swamp out any subtle changes and benefits in the pulp zone with regard to surface chemistry.

Galvanic interactions are occurring when mild steel milling is used, and the addition of nitrogen hinders these interactions. No evidence of a galvanic protection mechanism, where pyrrhotite is favourably oxidised over pentlandite, was found. During tests measuring the level of surface hydroxides, it was observed that for mild steel milling, the level of hydroxides on nickel and iron minerals were significantly higher than for those observed for stainless steel milling. This indicates that the mineral - media galvanic interactions are occurring during mild steel milling, and that the highly reactive pyrrhotite and pentlandite minerals are being oxidised as a result of them.

Additionally, the use of nitrogen on pulp milled in mild steel media, in the presence of collector and activator, resulted in significantly lower levels of surface hydroxides removed by EDTA. This indicates that with the addition of nitrogen, the level of surface hydroxides on the mineral surface is decreased via displacement. It is possible that this could be as a result of enhanced collector-mineral interactions in the presence of nitrogen and subsequent displacement of loosely bonded hydroxy coatings by MX species (especially in the case of pentlandite, where a recovery increase was observed). Additionally, if galvanic

interactions continue to occur in the pulp after milling, and during conditioning, it can be argued that the nitrogen addition serves to hinder galvanic interactions and therefore decrease the level of surface hydroxides present on the minerals.

ORP and DO measurements, while providing useful general information about the pulp chemistry, are not enough to predict flotation performance.

This is demonstrated by the fact that tests displaying similar pulp chemistry measurements of ORP and DO produced different metallurgical performances as measured by recovery and grade. This indicates that the ORP and DO, while being useful parameters, do not fully characterise the pulp chemistry, and other measurements and effects need to be considered (i.e. ions in solution, mineral potential measurements, etc.)

Investigations of the effect of nitrogen, both on the mineral-activator-collector interaction and on the levels of mineral surface oxidation, show interesting phenomena that need to be studied via more direct approaches.

In this regard, the results of the indirect measurement techniques used in this study justify further investigation of a more direct nature. FTIR (Fourier Transform Infrared Spectroscopy) or TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy) techniques are recommended for further investigation of the role of nitrogen on flotation.

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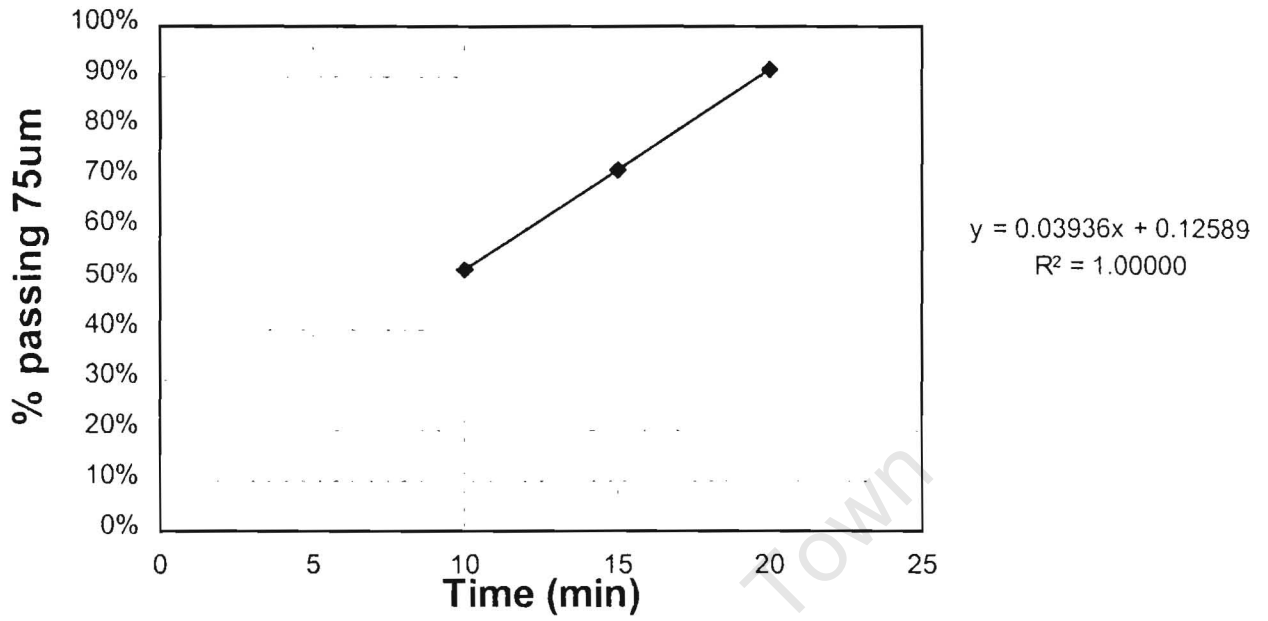
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APPENDIX A

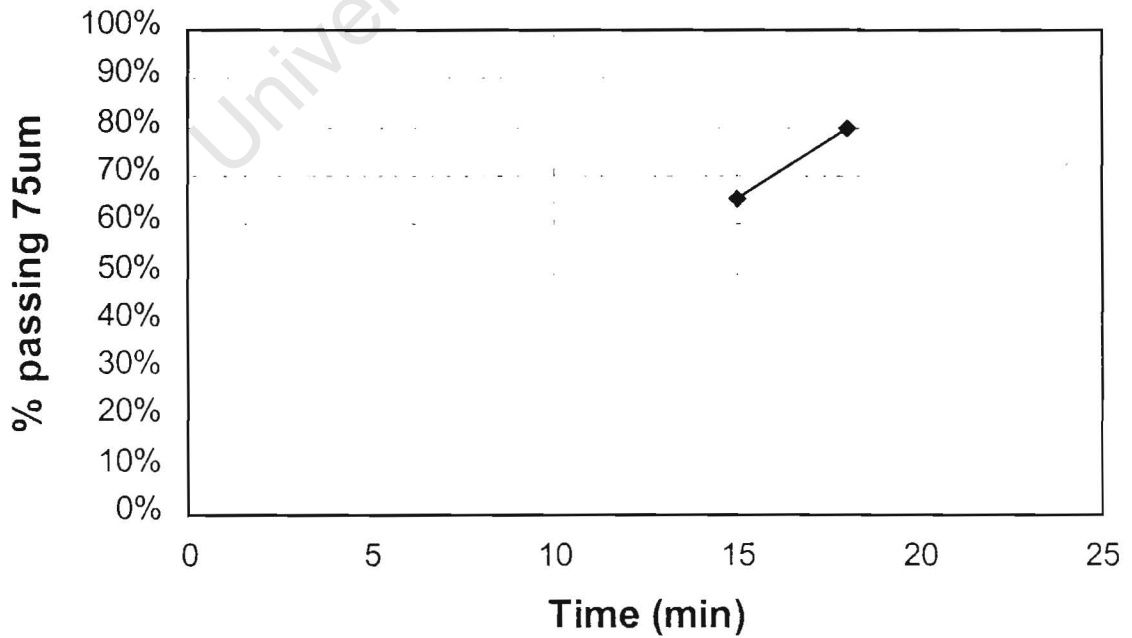
Milling Curves

University of Cape Town

Milling Curve (Stainless Steel rods)



Milling Curve (Mild Steel rods)

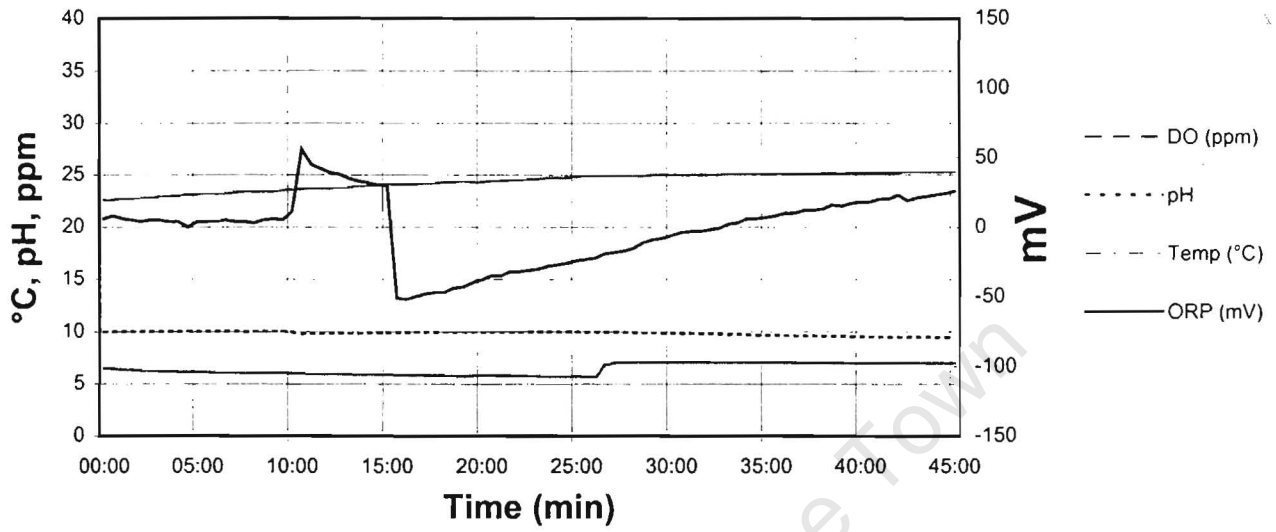


APPENDIX B

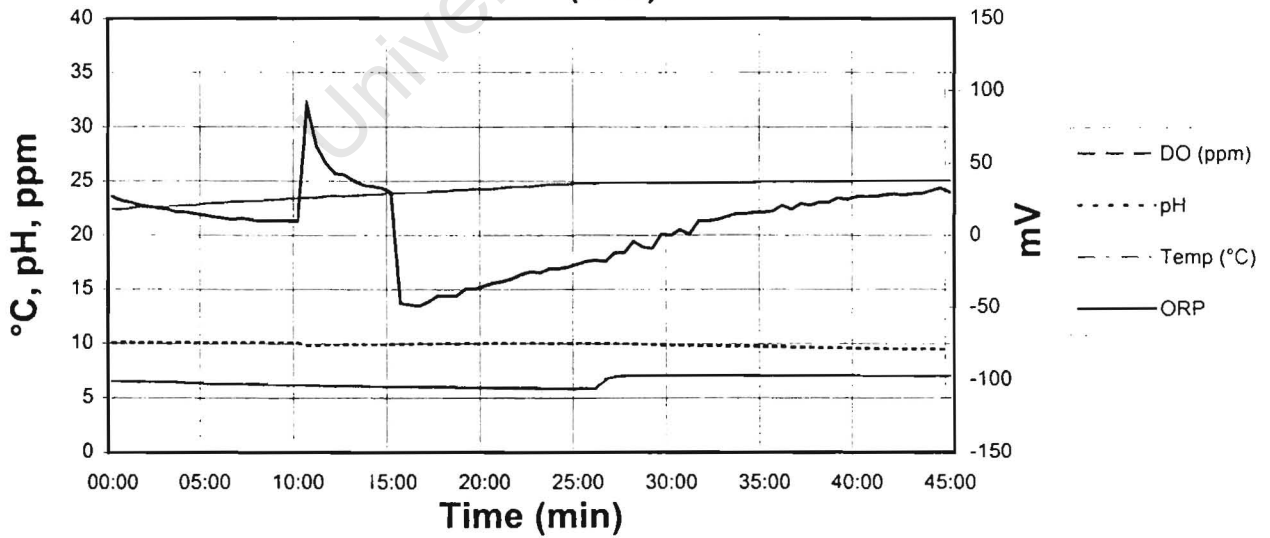
Pulp Chemistry Profiles

University of Cape Town

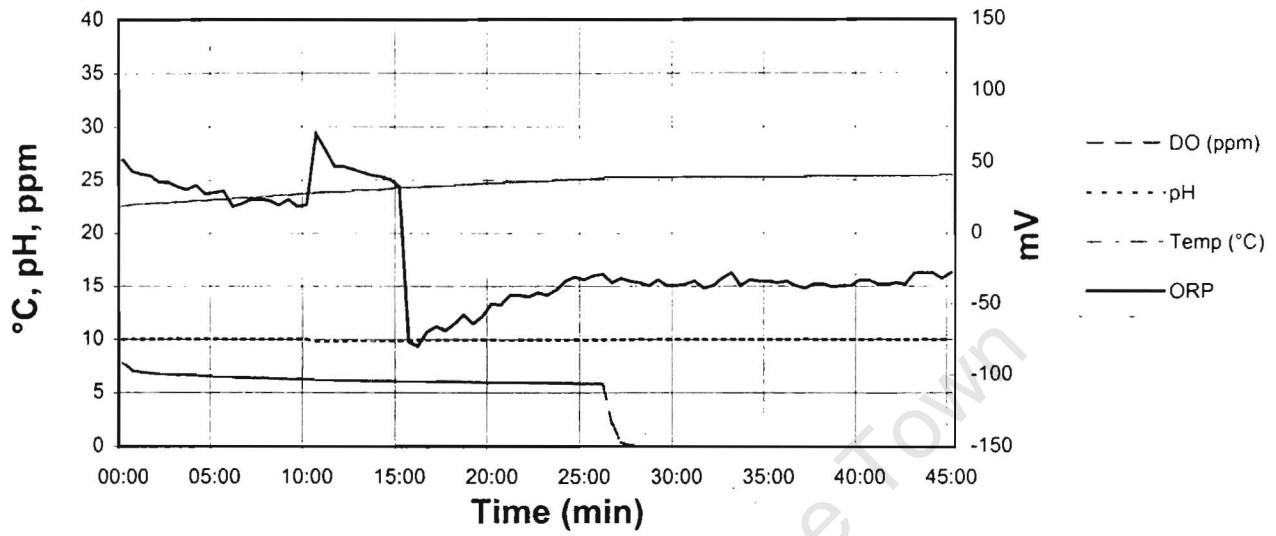
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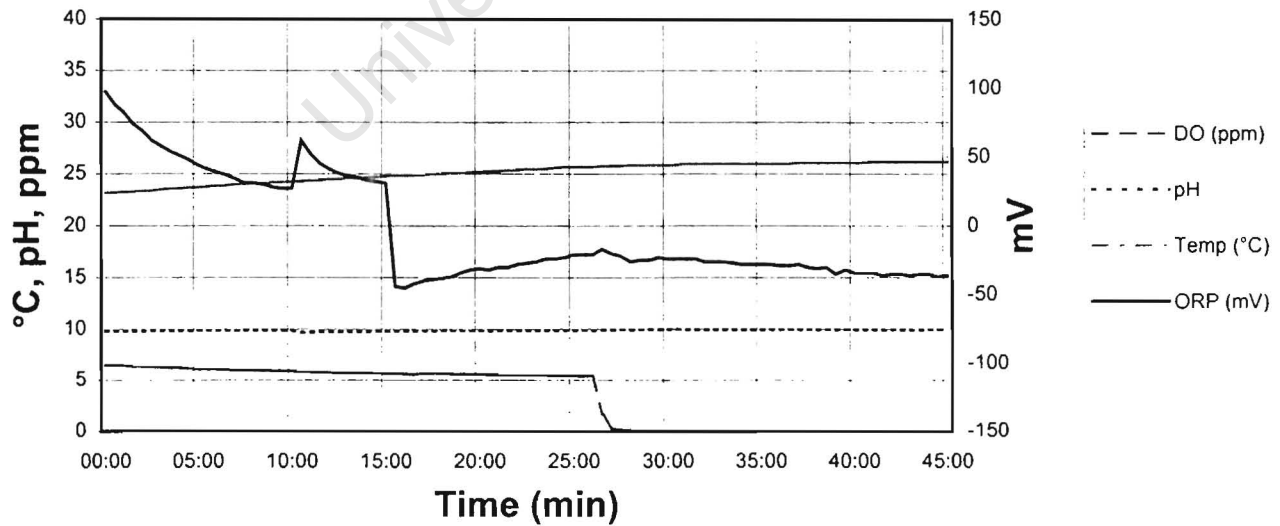
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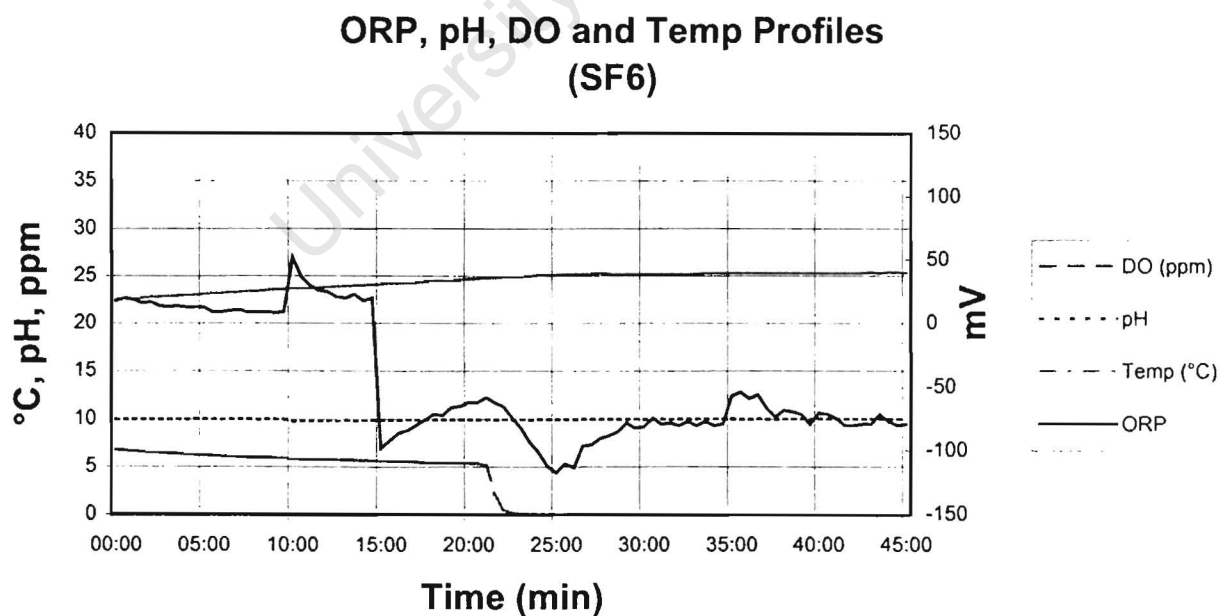
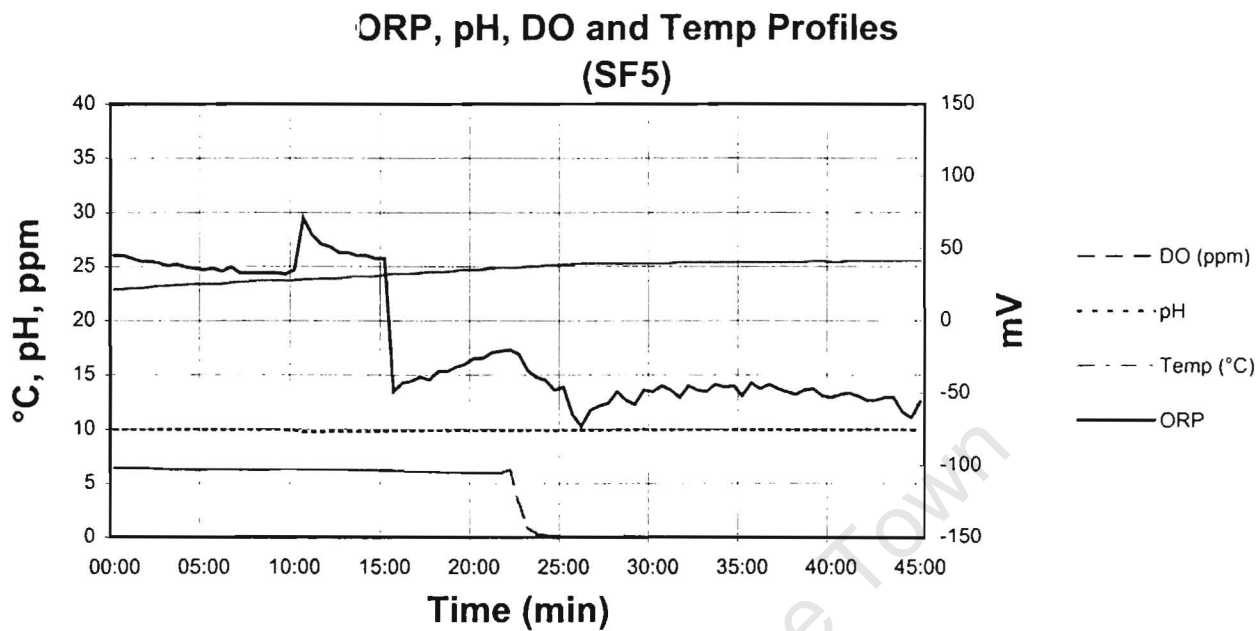


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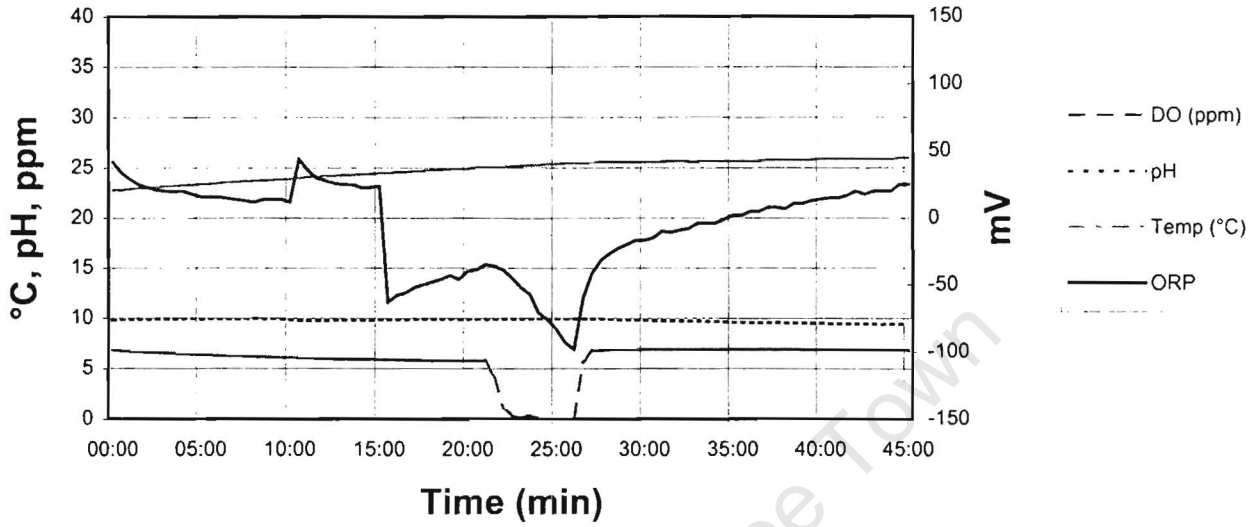


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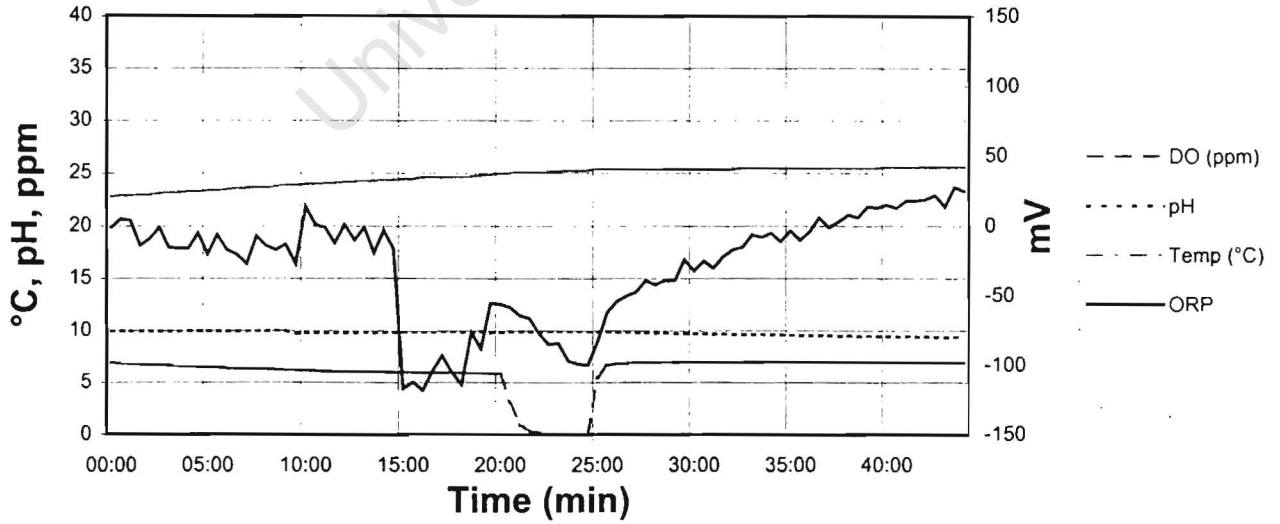




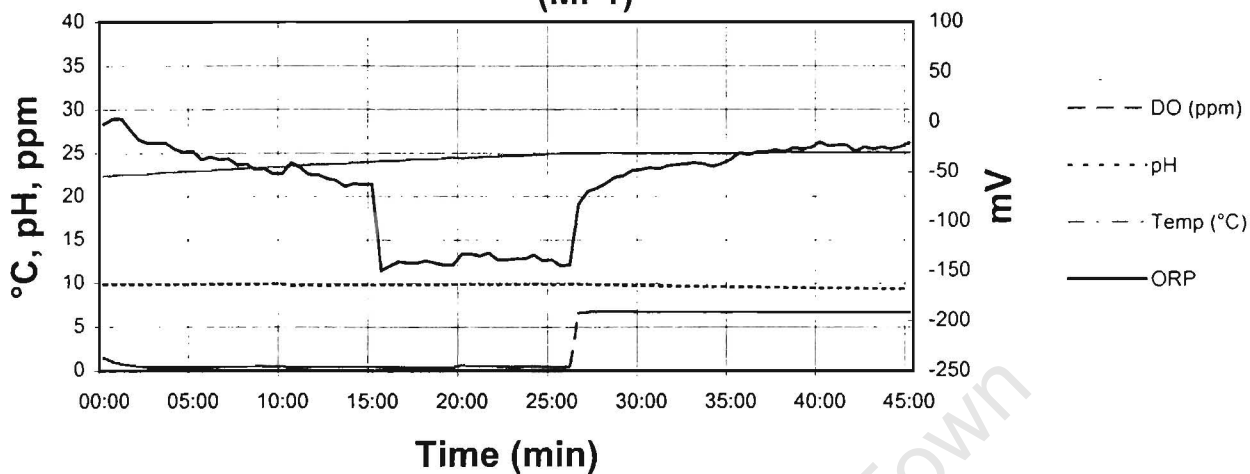
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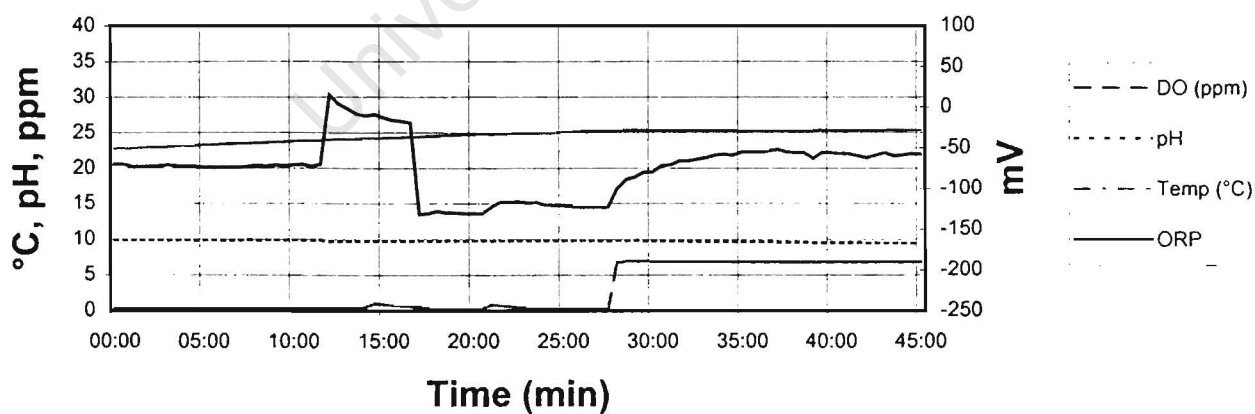
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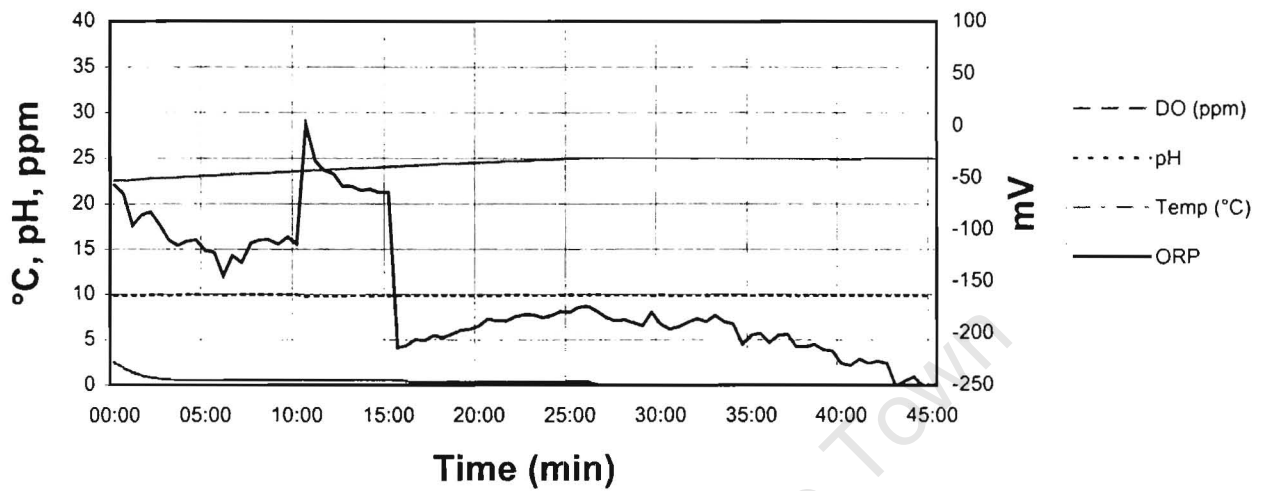
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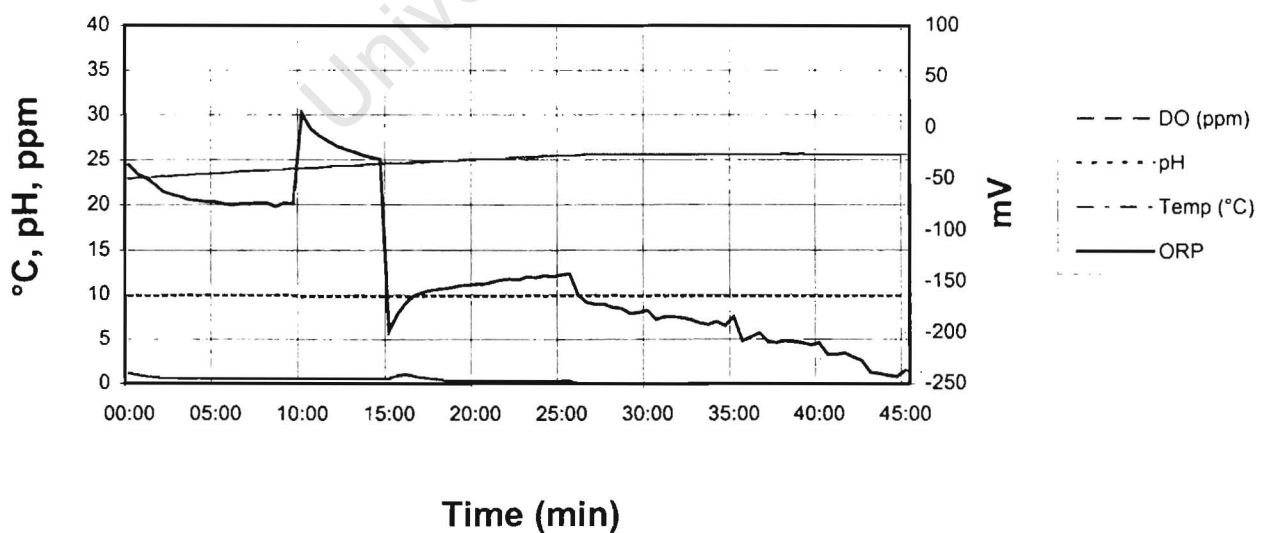
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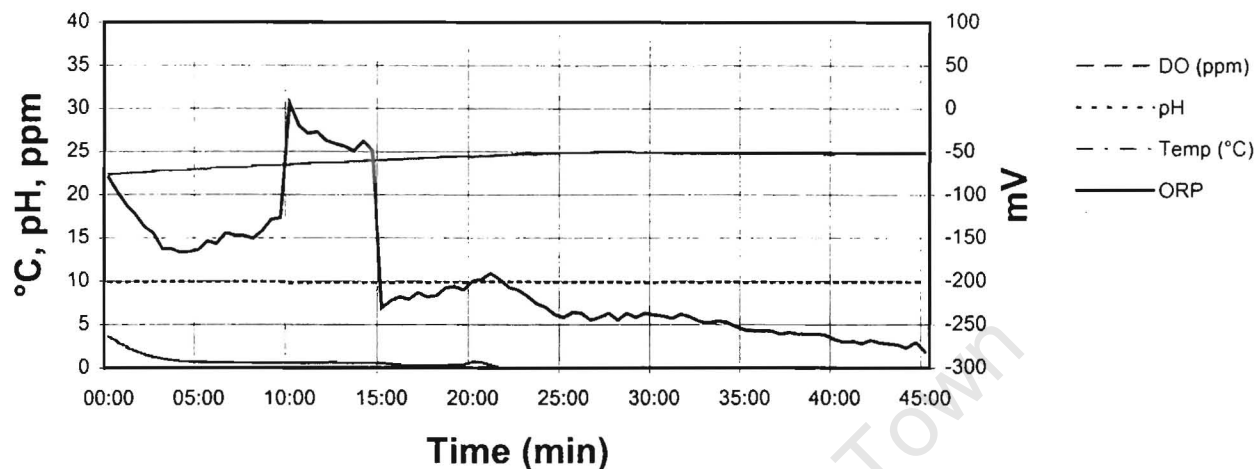
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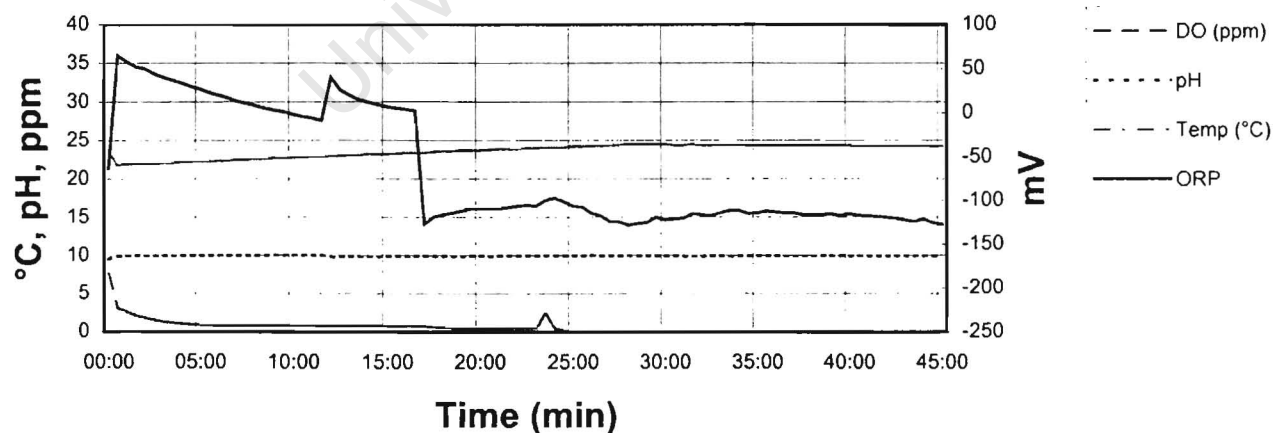
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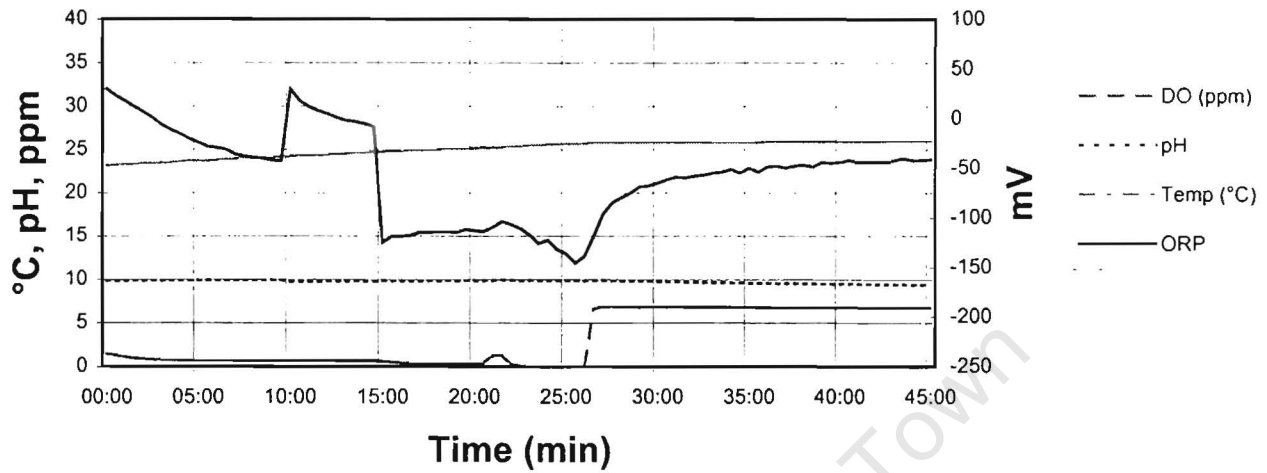
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(MF5)



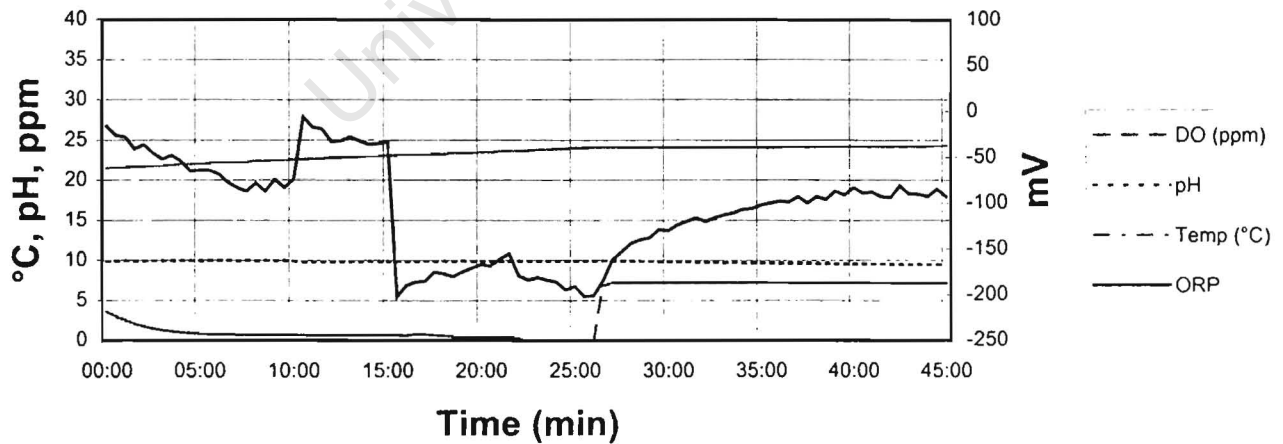
ORP, pH, DO and Temp Profiles
(MF6)



ORP, pH, DO and Temp Profiles
(MF7)



ORP, pH, DO and Temp Profiles
(MF8)



APPENDIX C

Copper Balance

University of Cape Town

EDTA extracted copper			Copper added			
Test No	Copper extracted by EDTA for mass treated (mg/sample)	Copper not from ore (i.e subtract baseline test, 'S 0') mg/sample)	CuSO ₄ .5H ₂ O added total (mg)	mmoles CuSO ₄ .5H ₂ O added	mg copper added	copper added per sample
S 1	0.08027	0.05266	1.68	0.0067	0.4306	0.0742
S 2	0.04732	0.01972	0.89	0.0036	0.2281	0.0323
S 3	0.06990	0.04230	1.92	0.0077	0.4921	0.0648
S 4	0.04498	0.01737	0.96	0.0038	0.2461	0.0324
S 0	0.02761	0.00000	0	0.0000	0.0000	0.0000

Final Copper Balance			
Test No	Normalised Extracted copper (mg/sample)	Copper added (mg/sample)	% removed
S 1	0.05266	0.0742	71%
S 2	0.01972	0.0323	61%
S 3	0.04230	0.0648	65%
S 4	0.01737	0.0324	54%
S 0	0.00000	0.0000	

APPENDIX D

**Examples of statistical
analyses: ANOVA and t-Test**

University of Cape Town

Sample Calculation of Statistical Analysis:

t -Test to assess the significance of effect of nitrogen conditioning after milling with stainless steel media

	Nickel recovery	
	STD	NA
x_1	57.95	73.13
x_2	56.57	73.09
x_3		
x_{mean}	57.26	73.11
s_i	0.976	0.028
n_i	2	2
Pooled variance (s^2)	0.476	
s	0.690	
t	-22.961	
Tdist (3 dof, 1 tailed)	0.001	
Significance level	99.9%	

Effect of nitrogen as conditioning gas and flotation gas after milling with stainless steel media: ANOVA analysis:

Nickel Recovery (effect of N_2 cond/flot with SS media)

	Expt	Data	Col. 1	Col. 2	Col. 3	Effects	SS
STD	1	58.0	131.06	251.81	494.79		
NA	a	73.1	120.75	242.98	11.97	2.99	17.91
NF	b	65.5	129.7	4.85	-26.73	-6.68	89.31
NA.NF	ab	55.2	113.28	7.12	-51.39	-12.85	330.12
STD(ii)	c	56.6	15.12	-10.31	-8.83	-2.21	9.75
NA(ii)	ac	73.1	-10.27	-16.42	2.27	0.57	0.64
NF(ii)	bc	61.4	16.56	-25.39	-6.11	-1.53	4.67
NA.NF(ii)	abc	51.9	-9.44	-26	-0.61	-0.15	0.05

Source of variation		Sum of Squares	DOF	Mean Square	F(j,N,jD) $F_{1,4}$	Prob.point (F-dist)	Prob level %	Significance
Main Effects	A	17.91	1	17.91	4.7	0.09	90.5	*
	B	89.31	1	89.31	23.7	0.01	99.2	****
	AB	330.12	1	330.12	87.4	0.00	99.9	****
Interactions	C	9.75	1	9.75				
	AC	0.64	1	0.64				
	BC	4.67	1	4.67				
	ABC	0.05	1	0.05				
TOTALS		452.4	7					
RESIDUAL ERROR (est. from expts, c,ac,bc,abc)					3.78			

A = Conditioning gas, B = Flotation Gas, AB = interaction, C = Replicates

APPENDIX E

Detailed Results of Flotation Tests

University of Cape Town

SS, NA (i)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered	
1	Conc. 1	11.40	11.4	69.10	69.10	3.34	38.08	38.08	3.34	48.46	12.02	136.98	136.98	12.02	4.93	6.55	74.67	74.67	6.55	38.29	
3	Conc. 2	5.35	16.75	49.99	119.09	2.04	10.90	48.98	2.92	62.34	15.14	81.01	217.98	13.01	7.84	5.43	29.04	103.71	6.19	53.17	
5	Conc. 3	3.52	20.27	8.42	127.51	1.28	4.49	53.48	2.64	68.05	13.29	46.80	264.78	13.06	9.52	4.45	15.66	119.36	5.89	61.20	
10	Conc. 4	6.89	27.16	74.38	201.89	0.53	3.68	57.15	2.10	72.73	10.85	74.78	339.56	12.50	12.21	2.42	16.68	136.04	5.01	69.75	
20	Conc. 5	7.51	34.67	75.11	277.00	0.2	1.73	58.88	1.70	74.93	8.6	64.30	403.86	11.65	14.53	0.9	6.52	142.56	4.11	73.09	
	Tails	1006.1						78.58	mass bal.	96.25			2780.03	mass bal.	104.63			195.04	mass bal.	120.13	
	Feed	1040.8																			
	PI 211					MF Grade	0.08	CF Grade	0.08		MF Grade	2.55	CF Grade	2.67		MF Grade	0.16	CF Grade	0.19		
						MT Grade	0.02	CT Grade	0.02		MT Grade	2.36	CT Grade	2.24		MT Grade	0.05	CT Grade	0.02		

SS, NA (ii)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered	
1	Conc. 1	1.45	1.45	0.00	0.00	7.46	10.81	10.81	7.46	14.86	21.28	30.85	30.85	21.28	1.22	6.48	9.40	9.40	6.48	5.10	
3	Conc. 2	5.86	7.31	37.86	37.86	5.02	29.40	40.22	5.50	55.25	19.28	112.95	143.80	19.67	5.70	7.27	42.59	51.99	7.11	28.23	
5	Conc. 3	4.48	11.79	18.13	55.99	2.11	9.44	49.66	4.21	68.22	16.21	72.63	216.43	18.36	8.58	7.14	32.01	84.00	7.12	45.62	
10	Conc. 4	8.10	19.89	70.95	126.95	1.17	9.52	59.18	2.98	81.29	13.79	111.71	328.14	16.50	13.02	4.87	39.48	123.48	6.21	67.06	
20	Conc. 5	10.84	30.73	112.71	239.66	0.3	2.86	62.04	2.02	85.22	8.7	94.47	422.60	13.75	16.76	1.0	11.19	134.67	4.38	73.13	
	Tails	984.6						72.80	mass bal.	99.41			2521.22	mass bal.	91.55			184.15	mass bal.	101.22	
	Feed	1015.3																			
	PI 213					MF Grade	0.07	CF Grade	0.07		MF Grade	2.71	CF Grade	2.48		MF Grade	0.18	CF Grade	0.18		
						MT Grade	0.01	CT Grade	0.01		MT Grade	2.13	CT Grade	2.37		MT Grade	0.05	CT Grade	0.05		

STD, SS (i)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered	
1	Conc. 1	0.33	0.33	0.00	0.00	13.10	4.32	4.32	13.10	5.84	24.88	8.21	8.21	24.88	0.36	6.01	1.98	1.98	6.01	0.93	
3	Conc. 2	3.15	3.48	24.51	24.51	6.18	19.47	23.79	6.84	32.17	19.47	61.34	69.55	19.98	3.01	7.60	23.94	25.92	7.45	12.16	
5	Conc. 3	2.63	6.11	8.30	32.81	2.30	6.06	29.85	4.88	40.37	16.06	42.23	111.78	18.29	4.84	7.27	19.12	45.04	7.37	21.13	
10	Conc. 4	6.10	12.21	46.94	79.75	3.12	19.03	48.88	4.00	66.11	18.72	114.18	225.96	18.51	9.79	7.57	46.17	91.21	7.47	42.78	
20	Conc. 5	9.65	21.87	90.56	170.31	0.7	7.14	56.02	2.56	75.76	12.6	122.08	348.04	15.91	15.08	3.4	32.37	123.58	5.65	57.97	
	Tails	896.1						73.94	mass bal.	98.61			2308.33	mass bal.	73.65			213.19	mass bal.	109.25	
	Feed	938.0																			
	PI 204					MF Grade	0.08	CF Grade	0.08		MF Grade	3.34	CF Grade	2.46		MF Grade	0.21	CF Grade	0.23		
						MT Grade	0.02	CT Grade	0.02		MT Grade	2.19	CT Grade	3.11		MT Grade	0.10	CT Grade	0.08		

STD, SS (ii)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc.Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered	
1	Conc. 1	0.47	0.47	0.00	0.00	7.99	3.76	3.76	7.99	7.58	23.11	10.86	10.86	23.11	0.33	5.97	2.81	2.81	5.97	1.44	
3	Conc. 2	5.12	5.59	21.80	21.80	4.27	21.88	25.63	4.59	51.75	19.89	101.83	112.69	20.16	3.43	6.80	34.82	37.63	6.73	19.34	
5	Conc. 3	3.98	9.57	17.22	39.02	2.26	9.01	34.64	3.62	69.93	17.13	68.16	180.85	18.90	5.50	7.11	28.28	65.91	6.89	33.88	
10	Conc. 4	6.30	15.87	51.57	90.59	0.84	5.26	39.90	2.51	80.55	14.34	90.31	271.16	17.09	8.25	5.27	33.18	99.10	6.24	50.94	
20	Conc. 5	8.34	24.21	101.62	192.21	0.2	1.52	41.42	1.71	83.62	10.3	85.54	356.70	14.73	10.85	1.3	10.97	110.06	4.55	56.57	
	Tails	835.8						49.53	mass bal.	90.26			3287.46	mass bal.	124.05			194.55	mass bal.	126.17	
	Feed	880.0																			
	PI 206					MF Grade	0.08	CF Grade	0.06		MF Grade	3.01	CF Grade	3.74		MF Grade	0.18	CF Grade	0.22		
						MT Grade	0.01	CT Grade	0.02		MT Grade	3.51	CT Grade	2.74		MT Grade	0.10	CT Grade	0.05		

SS, NF (i)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered	
2	Conc. 1	1.21	1.21	0.00	0.00	8.30	10.04	10.04	8.30	12.11	18.78	22.73	22.73	18.78	0.84	4.63	5.60	5.60	4.63	2.92	
3.5	Conc. 2	2.14	3.35	18.60	18.60	3.49	7.48	17.52	5.23	21.13	14.93	31.94	54.67	16.32	2.01	6.05	12.94	18.54	5.54	9.67	
5.5	Conc. 3	3.88	7.23	5.59	24.19	4.52	17.52	35.05	4.85	42.26	16.91	65.61	120.28	16.64	4.42	7.66	29.74	48.28	6.68	25.16	
10	Conc. 4	10.06	17.29	99.90	124.09	2.08	20.95	56.00	3.24	67.53	13.41	134.88	255.17	14.76	9.39	6.45	64.88	113.16	6.54	58.98	
20	Conc. 5	10.11	27.4	153.82	277.91	0.2	2.50	58.49	2.13	70.54	6.6	66.31	321.48	11.73	11.83	1.2	12.51	125.67	4.59	65.51	
	Tails	1006.7						82.93	mass bal.	90.69			2718.47	mass bal.	87.36			191.85	mass bal.	95.16	
	Feed	1034.1																			
	PI 208							MF Grade	0.09	CF Grade	0.08		MF Grade	3.01	CF Grade	2.63		MF Grade	0.19	CF Grade	0.19
								MT Grade	0.02	CT Grade	0.03		MT Grade	2.38	CT Grade	2.77		MT Grade	0.07	CT Grade	0.08

SS, NF (ii)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered	
1	Conc. 1	2.40	2.4	10.42	10.42	7.51	18.04	18.04	7.51	22.84	16.02	38.45	38.45	16.02	1.42	6.37	15.29	15.29	6.37	8.69	
3	Conc. 2	3.19	5.59	29.16	39.58	2.69	8.59	26.63	4.76	33.72	11.51	36.71	75.16	13.44	2.77	6.04	19.28	34.57	6.18	19.66	
5	Conc. 3	4.24	9.83	16.97	56.55	4.24	18.00	44.62	4.54	56.52	11.88	50.37	125.53	12.77	4.63	6.87	29.15	63.71	6.48	36.23	
10	Conc. 4	8.42	18.25	87.34	143.89	1.13	9.53	54.16	2.97	68.59	7.55	63.56	189.08	10.36	6.97	4.11	34.64	98.36	5.39	55.94	
20	Conc. 5	9.50	27.75	129.85	273.74	0.3	2.54	56.70	2.04	71.81	4.7	44.69	233.77	8.42	8.62	1.0	9.53	107.89	3.89	61.36	
	Tails	1099.4						78.95	mass bal.	99.57			2711.40	mass bal.	95.23			175.84	mass bal.	111.34	
	Feed	1127.2																			
	PI 210							MF Grade	0.07	CF Grade	0.07		MF Grade	2.53	CF Grade	2.41		MF Grade	0.14	CF Grade	0.16
								MT Grade	0.02	CT Grade	0.02		MT Grade	2.25	CT Grade	2.38		MT Grade	0.06	CT Grade	0.05

SS, NA, NF (i)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered	
1	Conc. 1	2.23	2.23	15.66	15.66	5.27	11.75	11.75	5.27	21.97	17.18	38.32	38.32	17.18	1.56	5.26	11.73	11.73	5.26	8.56	
3	Conc. 2	4.14	6.37	40.50	56.16	3.78	15.64	27.39	4.30	51.23	16.84	69.74	108.05	16.96	4.39	6.27	25.97	37.70	5.92	27.52	
5	Conc. 3	2.42	8.79	0.84	57.00	2.04	4.93	32.33	3.68	60.45	13.89	33.62	141.67	16.12	5.76	5.10	12.34	50.04	5.69	36.53	
10	Conc. 4	5.83	14.62	68.24	125.24	1.38	8.05	40.38	2.76	75.51	11.00	64.11	205.78	14.08	8.36	3.48	20.27	70.31	4.81	51.34	
20	Conc. 5	6.94	21.56	117.91	243.15	0.2	1.36	41.74	1.94	78.05	7.0	48.92	254.70	11.81	10.35	0.8	5.35	75.66	3.51	55.24	
	Tails	941.3						53.48	mass bal.	90.82			2461.72	mass bal.	87.01			136.96	mass bal.	84.67	
	Feed	962.9																			
	PI 207							MF Grade	0.06	CF Grade	0.06		MF Grade	2.94	CF Grade	2.56		MF Grade	0.17	CF Grade	0.14
								MT Grade	0.01	CT Grade	0.02		MT Grade	2.34	CT Grade	2.74		MT Grade	0.07	CT Grade	0.09

SS, NA, NF (ii)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered	
1	Conc. 1	4.72	4.72	21.06	21.06	4.85	22.89	22.89	4.85	34.79	16.17	76.34	76.34	16.17	2.73	4.73	22.30	22.30	4.73	14.05	
3	Conc. 2	7.85	12.57	72.68	93.74	2.52	19.74	42.64	3.39	64.80	12.49	98.02	174.36	13.87	6.24	4.02	31.53	53.83	4.28	33.90	
5	Conc. 3	4.37	16.94	23.55	117.29	1.00	4.39	47.03	2.78	71.47	9.69	42.36	216.72	12.79	7.75	2.89	12.63	66.46	3.92	41.86	
10	Conc. 4	7.11	24.05	79.14	196.43	0.56	3.95	50.98	2.12	77.48	7.78	55.30	272.02	11.31	9.73	1.59	11.27	77.73	3.23	48.96	
20	Conc. 5	10.36	34.41	159.09	355.52	0.1	1.32	52.30	1.52	79.49	6.4	65.79	337.81	9.82	12.08	0.5	4.71	82.44	2.40	51.92	
	Tails	1074.7						65.80	mass bal.	101.32			2796.10	mass bal.	103.05			158.78	mass bal.	88.58	
	Feed	1109.1																			
	PI 209							MF Grade	0.06	CF Grade	0.06		MF Grade	2.45	CF Grade	2.52		MF Grade	0.16	CF Grade	0.14
								MT Grade	0.01	CT Grade	0.01		MT Grade	2.29	CT Grade	2.21		MT Grade	0.07	CT Grade	0.09

MS, NA (i)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum mass Water	%Cu Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered
1	Conc. 1	17.74	17.74	95.04	95.04	2.70	47.90	47.90	2.70	70.23	15.25	270.54	270.54	15.25	8.83	5.73	101.59	101.59	5.73	62.33
5	Conc. 2	14.55	32.29	369.55	464.59	0.52	7.61	55.50	1.72	81.39	9.21	133.98	404.51	12.53	13.20	1.03	14.98	116.58	3.61	71.53
10	Conc. 3	12.25	44.54	0.00	464.59	0.21	2.60	58.11	1.30	85.20	7.09	86.83	491.34	11.03	16.04	0.35	4.29	120.86	2.71	74.16
20	Conc. 4	11.86	56.4	0.00	464.59	0.18	2.14	60.24	1.07	88.34	7.27	86.28	577.61	10.24	18.85	0.21	2.49	123.35	2.19	75.69
20	Conc. 5	0.00	56.4	0.00	464.59	0.0	0.00	60.24	1.07	88.34	0.0	0.00	577.61	10.24	18.85	0.0	0.00	123.35	2.19	75.69
	Tails	937.2						68.20	mass bal.	109.44			3063.75	mass bal.	90.19			162.98	mass bal.	101.56
	Feed	993.6																		
	PI 217					MF Grade	0.06	CF Grade	0.07		MF Grade	3.42	CF Grade	3.08		MF Grade	0.16	CF Grade	0.16	
						MT Grade	0.01	CT Grade	0.00		MT Grade	2.65	CT Grade	3.01		MT Grade	0.04	CT Grade	0.04	

MS, NA (ii)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum mass Water	%Cu Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered
1	Conc. 1	15.25	15.25	118.77	118.77	3.04	46.29	46.29	3.04	66.30	12.97	197.75	197.75	12.97	5.76	7.49	114.29	114.29	7.49	62.81
3.3	Conc. 2	10.62	25.87	101.30	220.07	0.60	6.37	52.67	2.04	75.43	11.08	117.67	315.42	12.19	9.19	1.22	12.96	127.24	4.92	69.93
5	Conc. 3	5.85	31.72	38.34	258.41	0.23	1.33	54.00	1.70	77.34	8.48	49.58	365.00	11.51	10.63	0.52	3.02	130.27	4.11	71.59
10	Conc. 4	11.23	42.95	138.41	396.82	0.13	1.51	55.50	1.29	79.49	8.10	91.00	456.00	10.62	13.28	0.32	3.57	133.84	3.12	73.55
20	Conc. 5	14.16	57.11	232.94	629.76	0.1	1.17	56.68	0.99	81.17	7.4	104.13	560.13	9.81	16.32	0.2	2.60	136.44	2.39	74.98
	Tails	999.9						69.82	mass bal.	93.63			3432.77	mass bal.	82.21			181.97	mass bal.	122.02
	Feed	1057.0																		
	PI 221					MF Grade	0.07	CF Grade	0.07		MF Grade	3.95	CF Grade	3.25		MF Grade	0.14	CF Grade	0.17	
						MT Grade	0.01	CT Grade	0.02		MT Grade	2.87	CT Grade	3.62		MT Grade	0.05	CT Grade	0.01	

STD, MS (i)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum mass Water	%Cu Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered
1	Conc. 1	10.44	10.44	51.89	51.89	3.54	36.99	36.99	3.54	54.18	18.86	196.86	196.86	18.86	4.96	6.69	69.87	69.87	6.69	37.76
3	Conc. 2	10.93	21.37	96.56	148.45	1.34	14.62	51.61	2.41	75.59	14.49	156.38	355.25	16.62	8.95	3.69	40.32	110.19	5.16	59.55
5	Conc. 3	6.22	27.59	50.12	198.57	0.46	2.88	54.49	1.97	79.81	10.91	67.89	423.13	15.34	10.66	1.72	10.69	120.88	4.38	65.33
10	Conc. 4	9.42	37.01	127.51	326.08	0.19	1.76	56.25	1.52	82.39	6.80	64.07	487.20	13.16	12.27	0.52	4.93	125.80	3.40	67.99
20	Conc. 5	8.55	45.56	123.49	449.57	0.2	1.67	57.92	1.27	84.84	7.5	64.55	551.75	12.11	13.90	0.3	2.47	128.27	2.82	69.33
	Tails	893.3						68.27	mass bal.	113.35			3970.54	mass bal.	125.92			185.03	mass bal.	90.01
	Feed	938.8																		
	PI 201					MF Grade	0.06	CF Grade	0.07		MF Grade	3.36	CF Grade	4.23		MF Grade	0.22	CF Grade	0.20	
						MT Grade	0.01	CT Grade	0.00		MT Grade	3.83	CT Grade	2.91		MT Grade	0.06	CT Grade	0.09	

STD, MS (ii)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum mass Water	%Cu Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc Wt x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered
1	Conc. 1	16.83	16.83	112.45	112.45	3.13	52.67	52.67	3.13	70.93	18.23	306.84	306.84	18.23	9.67	6.63	111.66	111.66	6.63	57.65
3	Conc. 2	9.83	26.66	95.84	208.29	0.75	7.36	60.04	2.25	80.84	13.12	128.96	435.80	16.35	13.73	2.64	25.95	137.61	5.16	71.05
5	Conc. 3	6.04	32.7	49.37	257.66	0.33	2.00	62.03	1.90	83.53	9.67	58.40	494.20	15.11	15.57	1.12	6.79	144.40	4.42	74.56
10	Conc. 4	11.11	43.81	140.85	398.51	0.16	1.74	63.77	1.46	85.88	8.27	91.91	586.12	13.38	18.47	0.48	5.33	149.73	3.42	77.31
20	Conc. 5	10.53	54.34	169.09	567.60	0.1	0.96	64.74	1.19	87.17	8.1	85.16	671.28	12.35	21.16	0.3	2.79	152.52	2.81	78.75
	Tails	863.7						74.26	mass bal.	90.05			3173.14	mass bal.	83.48			193.68	mass bal.	104.43
	Feed	938.0																		
	PI 203					MF Grade	0.09	CF Grade	0.08		MF Grade	4.05	CF Grade	3.38		MF Grade	0.20	CF Grade	0.21	
						MT Grade	0.01	CT Grade	0.02		MT Grade	2.90	CT Grade	3.62		MT Grade	0.05	CT Grade	0.04	

MS, NF (i)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered
1	Conc. 1	14.62	14.62	105.41	105.41	3.10	45.27	45.27	3.10	62.66	14.64	213.99	213.99	14.64	6.05	7.13	104.26	104.26	7.13	53.10
3	Conc. 2	13.02	27.64	137.91	243.32	0.69	9.03	54.30	1.96	75.16	9.37	121.98	335.96	12.15	9.50	2.66	34.62	138.89	5.02	70.73
5	Conc. 3	9.59	37.23	101.89	345.21	0.28	2.68	56.98	1.53	78.87	6.65	63.79	399.75	10.74	11.30	0.71	6.76	145.65	3.91	74.17
10	Conc. 4	15.62	52.85	222.07	567.28	0.13	2.07	59.04	1.12	81.73	6.07	94.88	494.64	9.36	13.99	0.30	4.61	150.26	2.84	76.52
20	Conc. 5	14.01	66.86	227.84	795.12	0.1	1.61	60.65	0.91	83.96	8.5	90.50	585.13	8.75	16.54	0.2	2.27	152.53	2.28	77.67
	Tails	982.8						72.24	mass bal.	111.41			3536.68	mass bal.	94.69			196.37	mass bal.	119.77
	Feed	1049.6																		
	PI 215					MF Grade	0.06	CF Grade	0.07		MF Grade	3.56	CF Grade	3.37		MF Grade	0.16	CF Grade	0.19	
						MT Grade	0.01	CT Grade	0.00		MT Grade	3.00	CT Grade	3.21		MT Grade	0.04	CT Grade	0.01	

MS, NF (ii)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered
1	Conc. 1	16.63	16.63	138.09	138.09	2.51	41.79	41.79	2.51	59.58	13.31	221.40	221.40	13.31	6.16	5.62	93.40	93.40	5.62	53.27
3	Conc. 2	9.46	26.09	94.25	232.34	0.79	7.46	49.24	1.89	70.21	9.06	85.73	307.13	11.77	8.55	2.69	25.44	118.84	4.55	67.78
5	Conc. 3	6.30	32.39	53.09	285.43	0.31	1.98	51.22	1.68	73.03	6.91	43.50	350.64	10.83	9.76	0.78	4.93	123.77	3.82	70.59
10	Conc. 4	10.58	42.97	147.04	432.47	0.17	1.78	53.00	1.23	75.58	5.72	60.52	411.16	9.57	11.44	0.35	3.75	127.52	2.97	72.74
20	Conc. 5	14.97	57.94	254.06	686.53	0.1	1.79	54.79	0.95	78.11	6.0	89.57	500.73	8.64	13.93	0.2	2.75	130.28	2.25	74.31
	Tails	998.7						70.14	mass bal.	100.95			3593.38	mass bal.	108.32			175.32	mass bal.	103.70
	Feed	1056.6																		
	PI 219					MF Grade	0.07	CF Grade	0.07		MF Grade	3.14	CF Grade	3.40		MF Grade	0.16	CF Grade	0.17	
						MT Grade	0.02	CT Grade	0.01		MT Grade	3.10	CT Grade	2.82		MT Grade	0.05	CT Grade	0.04	

MS, NA, NF (i)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered
1	Conc. 1	17.83	17.83	159.20	159.20	2.18	38.85	38.85	2.18	59.98	11.69	208.37	208.37	11.69	6.50	6.01	107.14	107.14	6.01	61.82
3	Conc. 2	7.55	25.38	88.30	247.50	0.52	3.95	42.81	1.69	66.08	7.02	52.99	261.36	10.30	8.15	1.44	10.86	118.00	4.65	68.08
5	Conc. 3	8.90	34.28	120.15	367.65	0.24	2.11	44.92	1.31	69.34	6.20	55.15	316.51	9.23	9.87	0.56	5.02	123.02	3.59	70.98
10	Conc. 4	13.19	47.47	212.99	580.64	0.15	1.93	46.85	0.99	72.32	5.96	78.55	395.06	8.32	12.32	0.30	3.90	126.92	2.67	73.23
20	Conc. 5	12.47	59.94	232.72	813.36	0.1	1.50	48.35	0.81	74.64	6.1	76.10	471.16	7.86	14.69	0.2	1.94	128.86	2.15	74.35
	Tails	977.9						64.78	mass bal.	97.56			3207.73	mass bal.	99.95			173.31	mass bal.	109.37
	Feed	1037.8																		
	PI 216					MF Grade	0.06	CF Grade	0.06		MF Grade	3.09	CF Grade	3.09		MF Grade	0.15	CF Grade	0.17	
						MT Grade	0.02	CT Grade	0.02		MT Grade	2.80	CT Grade	2.80		MT Grade	0.05	CT Grade	0.03	

MS, NA, NF (ii)

Time (min)	Concentrate Number	Weight Conc.	Cumul Mass	Mass Water	Cum. mass Water	%Cu Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Cu)	% Cu Recovered	%Fe Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Fe)	% Fe Recovered	% Ni Assay	Conc. Wt. x Assay	Cum. Wt. x Assay	Grade (%Ni)	% Ni Recovered
1	Conc. 1	15.68	15.68	129.64	129.64	2.79	43.78	43.78	2.79	62.00	15.01	235.32	235.32	15.01	6.50	7.58	118.92	118.92	7.58	65.23
3.3	Conc. 2	9.25	24.93	117.71	247.35	0.66	6.12	49.90	2.00	70.66	7.67	70.97	306.28	12.29	8.46	1.40	12.97	131.89	5.29	72.34
5	Conc. 3	5.07	30	48.37	295.72	0.24	1.24	51.14	1.70	72.42	6.40	32.46	338.75	11.29	9.35	0.57	2.89	134.79	4.49	73.93
10	Conc. 4	10.08	40.08	157.80	453.52	0.16	1.57	52.71	1.32	74.63	6.32	63.67	402.42	10.04	11.11	0.33	3.36	138.14	3.45	75.77
20	Conc. 5	14.78	54.86	255.33	708.85	0.1	1.93	54.64	1.00	77.37	5.7	84.43	486.84	8.87	13.44	0.2	3.02	141.16	2.57	77.43
	Tails	980.4						70.62	mass bal.	101.19			3621.61	mass bal.	114.71			182.32	mass bal.	115.63
	Feed	1035.3																		
	PI 220					MF Grade	0.07	CF Grade	0.07		MF Grade	3.05	CF Grade	3.50		MF Grade	0.15	CF Grade	0.18	
						MT Grade	0.02	CT Grade	0.02		MT Grade	3.20	CT Grade	2.72		MT Grade	0.04	CT Grade	0.02	

APPENDIX F

Error Calculations for EDTA complexation tests

University of Cape Town

EDTA (ul)	mg Fe/g	mg Cu/g	mg Ni/g
108	0.0030	0.00007	0.00022
108	0.0000	0.00003	0.00004
1080	0.0046	0.00016	0.00039
1080	0.0000	0.00017	0.00020
10800	0.1428	0.00125	0.00444
10800	0.1344	0.00138	0.00537

Above is a table showing the showing amount of metal extracted with varying EDTA dosage for duplicate tests.

NOTE: When the dosage of EDTA was low (108 and 1080 ul), all the metal was not being complexed, and very little metal was extracted. Given the limitations on equipment of reading such low values, and of the experimental procedure in duplicating such tests, the standard of repeatability of these tests were low. As the EDTA dosage was increased to a higher value (*tenfold increase* to 10800 ul), the technique gave more stable and reliable readings as mirrored in the data. It must be said that the high levels of gangue cause little confidence with regard to the measurement of copper and nickel minerals, while the abundance of iron (especially after mild steel milling), make the iron results more reliable (lower "noise to measurement" ratio). This can be seen in the table of errors for the various metals below.

EDTA dosage (ul)	Fe error	Cu error	Ni error
108	141%	62%	99%
1080	141%	6%	44%
10800	4%	7%	13%

Given the trend of decreasing standard deviation with increasing EDTA dosage present in the data above, and since a dosage slightly larger than 10800 was chosen for the experimental tests, we can safely conclude that the standard deviations will be at most equivalent to that calculated for the 10800 ul dosage tests.

APPENDIX G

Sample UV Absorbance Profile

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Absorbance at 330 nm	0.00
Absorbance at 270 nm	0.03
Absorbance at 301 nm	0.84
Midpoint range (baseline correction)	0.01
Difference (final absorbance)	0.83

